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GEOLOGY
OF THE
NON-METALLIC MINERAL DEPOSITS
OTHER THAN SILICATES

VOL. I
PRINCIPLES OF SALT DEPOSITION

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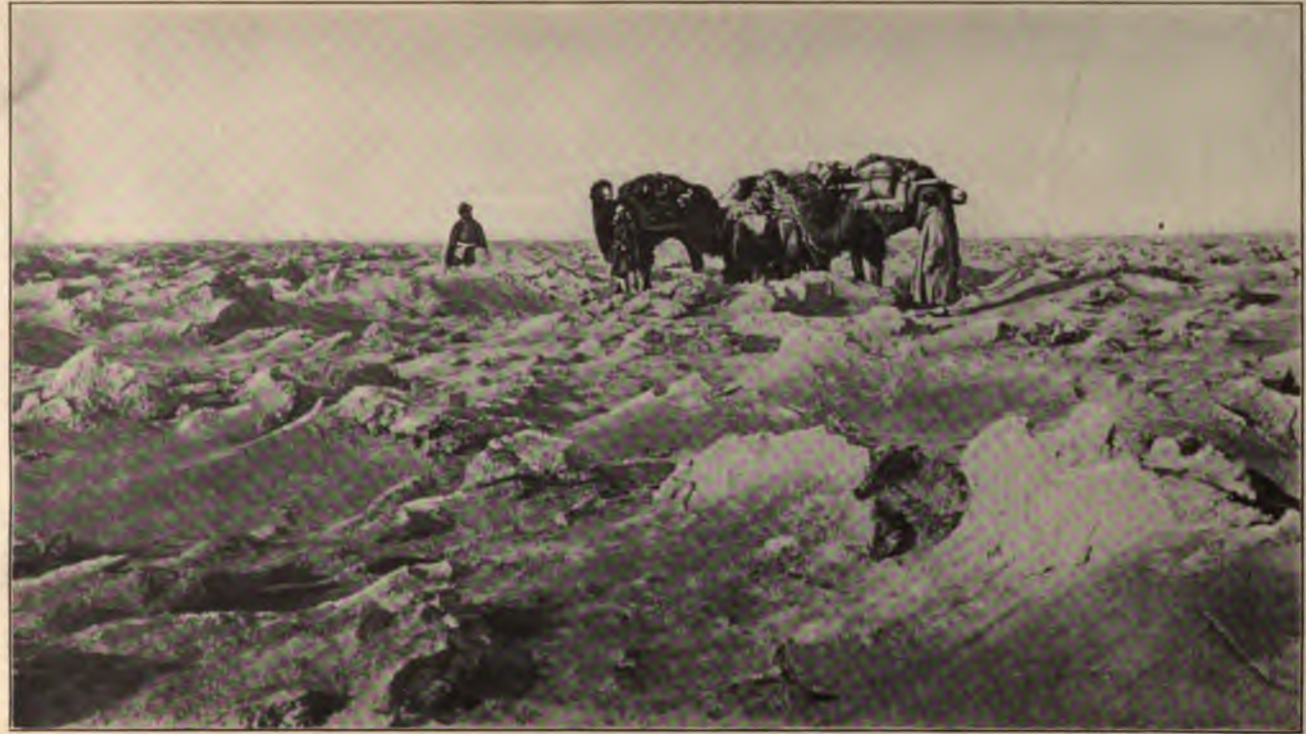

(Frontispiece)

THE SALT PLAIN OF LOP IN EASTERN TURKESTAN.
From a Photograph by Ellsworth Huntington. *(See page* 170)

GEOLOGY
OF THE
NON-METALLIC MINERAL DEPOSITS
OTHER THAN SILICATES

VOL. I
PRINCIPLES OF SALT DEPOSITION

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Whose Motto is "Thoroughness"

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My Beloved Teacher

WILLIAM OTIS CROSBY

EMERITUS PROFESSOR OF GEOLOGY

Who stands for all that is highest and best,
in Science, in Education and in Life.

On the occasion of the seventieth anniversary of his birth,
January 14, 1920.

PREFACE

This book is essentially a treatise on applied stratigraphy. As the title implies, it deals with non-metallic mineral deposits exclusive of silicates, but the hydrocarbons and some of the native elements are only incidentally considered. Their fuller treatment is reserved for a future work. The book might be designated a hand-book of salt-geology, if we use the term salt in a sufficiently broad sense to include nitrates, phosphates, borates and similar deposits.

The emphasis is laid upon the geological relationships of these deposits, and the chief endeavor has been to set forth our present understanding of the conditions under which such deposits are formed. To this end, the first volume is devoted to a study of deposits now forming or which have but recently been formed, and of the physical conditions which control such deposition. When these are understood it becomes possible to investigate the history of older deposits with some hope of success.

It has seemed advisable to preface the volume by a chapter summarizing the more important chemical principles which the student of salt-geology must keep in mind, and by a classification of such deposits. A second chapter, giving brief mineral characterizations and the general distribution of the substances dealt with, or incidentally mentioned in the book, serves as a glossary for ready reference. In considering lime and magnesia salts, and silica of organic origin, I have introduced a somewhat extended series of illustrations of modern and extinct organisms which are, or were chiefly active in the formation of such deposits, reducing the text to a mere commentary upon the illustrations. These illustrations will serve furthermore in connection with the stratigraphic chapters of the second volume, where of necessity, the types of organisms which serve as horizon markers, are more frequently referred to.

In the second volume the attempt has been made to apply the principles previously discussed, and to analyze the conditions under which the older deposits were formed. Throughout the endeavor has been to determine the criteria by which the search for valuable deposits in the stratified rocks might be guided. I offer no apologies for going much further afield than is generally done, in the discussion of stratigraphic principles, because I believe that all students of economic deposits in stratified rocks recognize the fundamental importance of such principles in the proper prosecution of their studies.

It is a pleasure to acknowledge the assistance of many friends in the preparation of this work. To Professor H. T. Beans of the department of chemistry in Columbia University, I am greatly indebted for looking over the general chemical chapter and making many helpful criticisms and suggestions. To Professor D. D. Jackson, head of the department of chemical engineering at Columbia, I am greatly indebted for calling my attention to the recent work on the origin of alkaline waters from zeolites. To my former colleagues in the geological department I am indebted for many helpful suggestions, and I wish especially to mention my indebtedness to Professor C. P. Berkey, to Messrs. R. J. Connelly and F. K. Morris and to Dr. J. J. Galloway. My friend Mr. Ernest Welleck has aided me greatly by his experience as chemist and as editorial writer in technical scientific journals. To my former student Miss Mary N. Welleck I am under special obligation for much careful work upon the manuscript, for extended search among the literature for facts and references, and for the preparation of a number of original illustrations as well as for redrawing a number of others for reproduction. To Dr. Ellsworth Hungington I am indebted for the photograph reproduced in the Frontispiece.

If the present work will aid in impressing upon students of economic deposits the importance of stratigraphy and palæogeography, I shall feel that one of the main objects of its preparation has been achieved.

NEW YORK,
January, 1920.

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GEOLOGY OF THE
NON-METALLIC MINERAL DEPOSITS
OTHER THAN SILICATES

VOL. I
PRINCIPLES OF SALT DEPOSITION

CHAPTER I

THE NATURAL SALTS, THEIR CHARACTER AND CLASSIFICATION

INTRODUCTORY CONSIDERATIONS

A salt may be briefly defined as a chemical compound formed by the union of an acid and a base. Many such combinations are known only in the chemical laboratory, having never been found to occur in a state of nature. With these we are not concerned in this book, though some may be mentioned incidentally. Others are found so rarely that they are chiefly of interest as mineralogical entities and would be considered by the student of salt deposits only in so far as they may throw light on the conditions of formation of the deposits in which they occur. Again, chemical compounds not strictly referable to salts, such as the oxides, especially the oxides of silicon or quartz (SiO_2), and of aluminum, and the hydrates of these elements deserve consideration in a treatise on natural salt deposits, especially when the economic aspect is emphasized. In this treatise, which is intended to consider salt deposits primarily in their geological relationships, we shall confine ourselves to three types of deposits:

1. Deposits formed from mineral substances held in solution in water either directly (*hydrogenic deposits*) thorrough the agencies of organisms (*biogenic deposits*).
2. Deposits formed directly from mineral substances in a state of vapor (*atmogenic deposits*). These include deposits from volcanic or other vapors.

brought about by cooling (sublimates), by the mixing of two gases or vapors, or the decomposition of gases or vapors by heat.

3. Deposits formed through alteration of other deposits by static metamorphism (*metagenic deposits*). Such alteration is brought about by the influence of solutions or by vapors and gases (pneumatolysis) which come in contact with previously existing minerals, acting as solvents and mineralizers, or by the action of solid on solid.

Substances formed by cooling and crystallization from a molten magma (pyrogenic deposits) are only incidentally considered. These are primarily complexes of many salts,[1] chiefly silicates, which are omitted from this treatise.

Before amplifying our discussion of salts and saline deposits, we shall briefly discuss the substances of which salts are composed. A knowledge of general chemistry is presupposed.

The Chemical Elements

Of the 83 elements now recognized by chemists, only a small number are of importance to the student of saline deposits. Eight of these elements make up about 99 per cent. of the solid surface portion of the earth as estimated by F. W. Clarke. These are marked by an asterisk in the following table. Fourteen others are of importance to the student of salt deposits as occurring in notable amounts in these compounds of the earth's crust. They are marked by a dagger in the table.

TABLE I.—THE CHEMICAL ELEMENTS WITH THEIR SYMBOLS, ATOMIC WEIGHTS AND VALENCES†

	Symbol	Atomic weight	Valences
*Aluminum (Aluminium)	Al	27.1	3
Antimony	Sb	120.2	3, 5
Argon	A	39.88	0
Arsenic	As	74.96	3, 5
†Barium	Ba	137.37	2
Beryllium (Glucinum)	Be	9.1	2
Bismuth	Bi	208.0	3, 5
†Boron	B	11.0	3

---

[1] For a classification of natural deposits on this basis, see the author's "Principles of Stratigraphy," Chapter VI.

† International Atomic Weights (1917). Valences are added by the author from various sources.

	Symbol	Atomic weight	Valences
†Bromine	Br	79.92	1, 3, 5, 7
Cadmium	Cd	112.40	2
Caesium	Cs	132.81	1
*Calcium	Ca	40.07	2
†Carbon	C	12.005	2, 4
Cerium	Ce	140.25	3, 4
†Chlorine	Cl	35.46	1, 3, 4, 5, 7
Chromium	Cr	52.0	2, 3, 6
Cobalt	Co	58.97	2, 3
Columbium (Niobium)	Cb	93.1	3, 5
Copper	Cu	63.57	1, 2
Dysprosium	Dy	162.5	3
Erbium	Er	167.7	3
Europium	Eu	152.0	
†Fluorine	F	19.0	1, 3, 7
Gadolinium	Gd	157.3	
Gallium	Ga	69.9	3
Germanium	Ge	72.5	2, 4
Glucinum (Beryllium)	Gl	9.1	2
Gold	Au	197.2	1, 3
Helium	He	4.00	0
Holmium	Ho	163.5	
†Hydrogen	H	1.008	1
Indium	In	114.8	3
†Iodine	I	126.92	1, 3, 5, 7
Iridium	Ir	193.1	2, 4, 6, 8
*Iron	Fe	55.84	2, 3, 4, 6
Krypton	Kr	82.92	0
Lanthanum	La	139.0	3, 4
Lead	Pb	207.20	2, 4
Lithium	Li	6.94	1
Lutecium	Lu	175.0	
*Magnesium	Mg	24.32	2
†Manganese	Mn	54.93	2, 3, 4, 6, 7
Mercury	Hg	200.6	1, 2
Molybdenum	Mo	96.0	2, 3, 4, 6
Neodymium	Nd	144.3	
Neon	Ne	20.2	0
Nickel	Ni	58.68	2, 3
Niobium (Columbium)	Nb	93.1	3, 5
Niton (Radium emanation)	Nt	222.4	
†Nitrogen	N	14.01	1, 3, 5
Osmium	Os	190.9	2, 4, 6, 8
*Oxygen	O	16.00	2
Palladium	Pd	106.7	2, 4, 8
†Phosphorus	P	31.04	3, 5

	Symbol	Atomic weight	Valences
Platinum	Pt	195.2	2, 4
*Potassium	K	39.10	1
Praseodymium	Pr	140.9	3
Radium	Ra	226.0	2
Rhodium	Rh	102.9	2, 4, 6, 8
Rubidium	Rb	85.45	1
Ruthenium	Ru	101.7	2, 4, 6, 8
Samarium	Sa	150.4	3
Scandium	Sc	44.1	3
Selenium	Se	79.2	2, 4, 6
*Silicon	Si	28.3	4
Silver	Ag	107.88	1
*Sodium	Na	23.00	1
†Strontium	Sr	87.63	2
†Sulphur	S	32.06	2, 4, 6
Tantalum	Ta	181.5	3, 5
Tellurium	Te	127.5	2, 4. 6
Terbium	Tb	159.2	3
Thallium	Tl	204.0	1, 3
Thorium	Th	232.4	4
Thulium	Tm	168.5	
Tin	Sn	118.7	2, 4
Titanium	Ti	48.1	3, 4
Tungsten	W	184.0	2, 4, 6
Uranium	U	238.2	2, 4, 6
Vanadium	V	51.0	2, 3, 5
Xenon	Xe	130.2	0
Ytterbium (Neoytterbium)	Yb	173.5	3
Yttrium	Yt	88.7	3
Zinc	Zn	65.37	2
Zirconium	Zr	90.6	4

Taking the Atmosphere, Hydrosphere and Lithosphere as a whole the number of elements which make up about 99 per cent. of the total are the following twelve, the percentage for each being added.[1]

Oxygen	50.02	Calcium	3.22	Hydrogen	0.95
Silicon	25.80	Sodium	2.36	Titanium	0.43
Aluminum	7.30	Potassium	2.28	Chlorine	0.20
Iron	4.18	Magnesium	2.08	Carbon	0,18

The Valences of Elements.—The proportions in which the atoms of a given element will combine with or displace those of another element is called its valence. Hydrogen is commonly taken as the standard for comparison, its valence being designated as 1. Any element which will enter into combination with, or displace one atom of hydrogen is called univalent (*i.e.*, it is equivalent to one atom of hydrogen), one combining with or displacing two atoms of hydrogen is called bivalent and so on. Some elements do not combine and these are called nonvalents.

---

[1] Clarke, F. W., Data of Geo-chemistry, 3d Ed., 1916, p. 34.

The types of valences are given in the following:

TABLE II.—VALENCE TYPES

Designation	Combination power	Symbol in terms of oxygen	Selected example
Nonvalent	0	R	Argon (A)
Univalent	1	R_2O	Sodium (Na)
Bivalent	2	RO	Calcium (Ca)
Trivalent	3	R_2O_3	Boron (B)
Tetravalent	4	RO_2	Silicon (Si)
Pentavalent	5	R_2O_5	Phosphorus (P) at times
Hexavalent	6	RO_3	Sulphur (S) at times
Heptavalent	7	R_2O_7	Manganese (Mn) at times
Octavalent	8	RO_4	Osmium (Os) at times

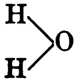
Discussion of Table.—The last four examples here given have other valences as well, these being as a rule more general. The nonvalent group includes the rare monatomic gases, apparently without power to combine. The valences of the commoner elements are given in the last column of Table 1.

A number of elements have more than one valence and so will form different types of combinations. As an example may be mentioned iron, which is multivalent, most frequently bi- and trivalent and so forms the following combinations with the bivalent element, oxygen. $Fe''O$, Fe'''_2O_3, the iron in the first case being bivalent (Fe'') when only one atom of each is required, and in the second case trivalent (Fe''') when two atoms of iron and three of oxygen are required. Still another valence for iron is shown in the combination FeS_2, the formula for pyrite and marcasite. The univalence of chlorine is shown by its combination with hydrogen as HCl while its heptavalence is shown by its combination with oxygen in Cl_2O_7.

Some elements which are tetra-, penta-, hexa- and heptavalent with reference to oxygen are tetra-, tri-, bi- and univalent, respectively, with reference to hydrogen. Thus, nitrogen which is pentavalent with reference to oxygen forming the combination N_2O_5 is trivalent with reference to hydrogen, forming the combination NH_3. Sulphur which has a maximum valence of 6 (hexavalent) with reference to oxygen, forming the combination SO_3, is bivalent with reference to hydrogen, forming the combination H_2S. Finally chlorine, which is heptavalent with reference to oxygen, forming the combination Cl_2O_7, is univalent with reference to hydrogen, forming the combination HCl.

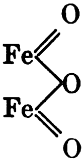
Graphic Expression of Valence.—We may represent the valence of an element by drawing about its symbol the number of lines (bonds) which corresponds to the valence which we assign to that element. Thus two lines indicate that the element is bivalent, three lines that it is trivalent, etc. The formulas may then be represented graphically as in the following examples:

$H_2O =$



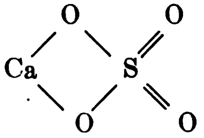
or $H-O-H$;

$Fe'''_2O_3 =$



or $O = Fe - O - Fe = O$

Calcium sulphate, $CaSO_4$, may be expressed as follows, Ca having two bonds, S six bonds and O two bonds:



Equivalent Weights.—In the study of solutions it is desirable to use the equivalent weight of the elements. This is found by dividing the atomic weight of that element by its valence, the result being the weight of that element which would displace one atomic weight of hydrogen or combine with one atomic weight of chlorine, or of any other univalent element.[1]

OCCURRENCE AND COMBINATION OF ELEMENTS

Many elements occur in nature in a gaseous or solid state or may be isolated as such in the laboratory, but by far the most common mode of occurrence of the elements is in combination with one another. Examples of uncombined elements occurring in nature are the rare monatomic gases, argon, helium, etc., which apparently never occur in a state of combination and the gases, oxygen and nitrogen, which make up the greater part of the atmosphere, but are also frequent in combination with other elements. Other elements which occasionally exist free in nature as gases but occur more commonly in a combined state are hydrogen and chlorine, both of which are readily isolated in the laboratory. Among the elements which occur in nature in a solid state are: carbon, sulphur and many metals such as gold, silver, copper, iron, platinum, etc.

The ordinary combinations of elements in nature constitute oxides, hydroxides, oxyhydroxides, acids and salts, both anhydrous and hydrous; these forming the essential mineral substances of the earth's crust.

Some of the acids are found in a free state in nature. Among them are hydrochloric and sulphuric acids, which occur in natural waters. An acid occurring as a mineral in a solid state is orthoboric acid (H_3BO_3) the mineral name of which is Sassolite. The hydroxides and oxyhydroxides constitute the bases of the salts, which they form by reacting with the acids. Such reaction is accompanied by the formation of water (see beyond). Besides these recognized combinations, there are dissociations of these, the existence of which is determined only in an indirect manner, and also mere theoretical entities, serviceable in the explanation of chemical changes. The first of these types are the *ions*, the second the *radicals*. A brief discussion of these may profitably precede the discussion of the higher compounds.

Ions.—When the higher chemical compounds (acids, salts, bases) are dissolved in water they are believed to be dissociated into two or more parts or ions which are either the elements or simple combinations of these or both. Thus the common salt, sodium chloride ($NaCl$), appears to be decomposed by water into its two ionized elements, sodium ($\overset{+}{Na}$) and chlorine ($\overset{-}{Cl}$), while sodium sulphate Na_2SO_4 is decomposed into the sodium ion ($2\overset{+}{Na}$) and the $\overset{-}{SO_4}$ ion. There is a marked behavior of these ions toward the passage of an electric current through the solution. Some of the ions will be attracted by the negative electrode and these are therefore regarded as charged with positive electricity. In the above examples sodium is the positive ion ($\overset{+}{Na}$) and chlorine and SO_4 are the negative ions ($\overset{-}{Cl}$) ($\overset{-}{SO_4}$). As the ions touch the electrodes their electricity is discharged and chemical reactions occur at the electrodes, their nature dependent on the solution. If the products of such electrolysis are gases, they may escape from the solution, if solids which are insoluble in the solution, *e.g.*, many metals, they will either cling to the electrodes, or fall to the bottom of the vessel as precipitates. If the products are soluble they are as a rule invisible. An ion may then be considered as an atom or group of atoms bearing an electrical charge and by virtue of this, being capable of existing in a separate state in the solution.

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[1] Smith, A. "Chemistry." Thus the equivalent weights of Al''', Ca'', Na' to one atomic weight of H = 1.008 are 9.03, 20 and 23 respectively. The first being one-third the atomic weight, the second one-half and the third the atomic weight.

As the electrical behavior of an element is not necessarily a fixed character, it may happen that an element is positive when compared with one, and negative when compared with another element. In the electrolysis of water, hydrogen behaves as the positive and oxygen as the negative element.

Radicals.—The term radical is applied to a group of atoms which occurs in the molecules of a number of different chemical compounds, or appears to remain intact throughout a series of transformations which a compound undergoes, in the formation of new molecular compounds. The combination (OH) is such a radical, uniting with various positive elements to form bases, as $K(OH)$, $Na(OH)$, etc. (see beyond), and with negative elements to form acids as $(HO)_2CO = H_2CO_3$. Again SO_4 is the radical of sulphuric acid, since it remains the same in uniting with various elements to form salts, as Na_2SO_4, $CaSO_4$, etc. As radicals are parts of molecules they are supposed to have free or uncombined valences which are different in the different radicals. Some of these are as follows:

Radical	Free valence	Example of combination
OH	1	$OH - H = H_2O$ $OH - K = K(OH)$ $\begin{matrix}OH\\OH\end{matrix}\!>Ca = Ca(OH)_2$
SO_4	2	$SO_4\!<\!\begin{matrix}H\\H\end{matrix}\Big\} = H_2SO_4$ $SO_4\!<\!\begin{matrix}Na\\Na\end{matrix}\Big\} = Na_2SO_4$ $SO_4 = Ca = CaSO_4$
SiO_4	4	$SiO_4\!<\!\begin{matrix}H\\H\\H\\H\end{matrix}\Bigg\} = H_4SiO_4$ $SiO_4\!<\!\begin{matrix}Mg\\Mg\end{matrix} = Mg_2SiO_4$

It must be remembered, however, that radicals are not known to exist in an uncombined state.

Oxides.—The simplest and most widespread combinations occurring in nature are the oxides, all of the elements except fluorine and some rare elements like those of the argon family (monatomic elements) forming compounds with oxygen. *Oxidation*, or the process of union of a substance with oxygen, may result by the abstraction of oxygen from the air, as in the burning of organic substances (carbon compounds) with the formation of CO_2, or the oxygen may be derived from an oxidizing agent, another compound, which gives up some of its oxygen and in so doing suffers *reduction*. Many oxides occur in nature, the commonest next to ice and water (H_2O) being the oxide of silicon (SiO_2) which as quartz and related mineral substances forms a conspicuous part of the earth's crust. Many oxides of metallic substances are found in nature, such as those of iron in hematite (Fe_2O_3), tin in cassiterite (SnO_2), zinc in zincite (ZnO), copper in cuprite (Cu_2O), aluminium in corundum (Al_2O_3), etc.

Hydroxides.—A hydroxide may be considered as the oxide of a metal or the positive substance which takes the place of a metal in which half of the oxygen atom has been tied to an atom of hydrogen, thus Na-O-H. Or it may be considered as a modification of the oxide of hydrogen or water (H_2O) in which half of the hydrogen has been replaced by a positive element or substance. Thus, by adding metallic sodium to water, the following reaction takes place:

$$Na_2 + 2H_2O = 2Na.OH + H_2$$

the hydrogen being set free. The hydroxide is sometimes spoken of as a hydrate and it can be expressed as the oxide of the metal with water. Thus sodium hydroxide, sometimes called sodium hydrate, may be expressed as the single molecule NaOH or as the double molecule $Na_2O + H_2O$; ($2NaOH = Na_2O + H_2O$). Sodium hydroxide NaOH, and potassium hydroxide KOH, are known in the arts as caustic soda and caustic potash, respectively. It is, however, desirable to restrict the term hydrate to a salt in which water of hydration is present, retaining the name hydroxide for the combination here discussed.

Oxyhydroxides.—By partial dehydration of the hydroxide, the oxyhydrate or better oxyhydroxide is produced. Thus the hydroxide of aluminum is $Al(OH)_3$ or $Al\begin{cases}-OH\\-OH,\\-OH\end{cases}$ while the oxyhydroxide is AlO(OH). This is commonly called the hydrous oxide of aluminum. Both occur in nature. The double molecule of the former may be resolved thus:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O \text{ (Gibbsite)}$$

while the double molecule of the latter may be resolved thus:

$$2AlO(OH) = Al_2O_3 + H_2O \text{ (Diaspore).}$$

Other examples of hydrous oxides or oxyhydroxides are:

FeO(OH) or Goethite. $Fe_4O_3(OH)_6$ or Limonite.

The double molecule of goethite may also be written $Fe_2O_3 + H_2O$. Limonite may be regarded as the mixture of the oxide Fe_2O_3 and the hydrate $Fe(OH)_3$, thus: $Fe_2O_3.2(Fe(OH)_3)$ or $Fe_2O_3.Fe_2(OH)_6$.

Hydroxyl.—The hydroxyl is the name applied to the (OH) radical, which is joined either to the metal or to the oxide. The (OH) radical is univalent, one bond of the bivalent oxygen being free, the other being joined to the univalent hydrogen thus -O-H. When the hydroxide is that of a univalent element only one hydroxyl is required, thus Na-(OH), but when the positive element is bi- or trivalent, the corresponding numbers of hydroxyls are required thus:

$$Al\begin{cases}-OH\\-OH\\-OH\end{cases} \quad \text{or} \quad Al \equiv (OH)_3.$$

When the hydroxyl is joined to an oxide of that element a smaller number of hydroxyls is as a rule required. Thus the aluminum oxyhydroxide requires only one hydroxyl, since in that case the aluminum has only one available bond, the other being tied to the oxygen thus:

$$O = Al - (OH) \text{ or } AlO(OH).$$

Acids.—This term is applied to combinations of negative elements, such as chlorine, carbon, sulphur, silica, etc., or their oxides, with hydrogen or with one or more hydroxyl radicals (OH), when the hydrogen can be replaced by some other positive element in the formation of a salt.

The following are some of the acids most of which enter into the combination of the salts discussed in this book:

HBr Hydrobromic acid	$H-Br + Aq$	
HCl Hydrochloric acid	$H-Cl + Aq$	
H_2S Hydrosulphuric acid	$H_2 = S + Aq$	
HNO_3 Nitric acid	$(OH) - N\left\{\begin{matrix}=\\=\end{matrix}\right\}O_2$	$(H_2O + N_2O_5 = 2HNO_3)$
H_2CO_3 Carbonic acid	$(OH)_2 = CO$	$(H_2O + CO_2 = H_2CO_3)$
H_2SO_4 Sulphuric acid	$(OH)_2 = SO_2$	$(H_2O + SO_3 = H_2SO_4)$
HPO_3 Metaphosphoric acid	$(OH) - PO_2$	$(H_2O + P_2O_5 = 2HPO_3)$
H_3PO_4 Orthophosphoric acid	$(OH)_3 \equiv PO$	$(3H_2O + P_2O_5 = 2H_3PO_4)$
$H_4P_2O_7$ Pyrophosphoric acid	$(OH)_4 ≣ P_2O_3$	$(2H_2O + P_2O_5 = H_4P_2O_7)$
$H_2B_4O_7$ Tetraboric acid	$(OH)_2 = B_4O_5$	$(H_2O + 2B_2O_3 = H_2B_4O_7)$
H_3BO_3 Orthoboric acid	$(OH)_3 \equiv B$	$(3H_2O + B_2O_3 = 2H_3BO_3)$
H_2SiO_3 Metasilicic acid	$(OH)_2 = SiO$	$(H_2O + SiO_2 = H_2SiO_3)$
H_4SiO_4 Orthosilicic acid	$(OH)_4 ≣ Si$	$(2H_2O + SiO_2 = H_4SiO_4)$
$H_4Si_3O_8$ Polysilicic acid	$(OH)_4 ≣ Si_3O_4$	$(2H_2O + 3SiO_2 = H_4Si_3O_8)$

All of the acids named except the first three may be considered as formed by the union of the oxides with water as indicated in the second half of the table. Where lower oxides occur, corresponding acids may often be formed. Thus, nitrogen trioxide (N_2O_3) forms nitrous acid (HNO_2) with water ($H_2O + N_2O_3 = 2HNO_2$), nitrous oxide (N_2O) forms hyponitrous acid ($(NOH)_2$) with water ($H_2O + N_2O = (NOH)_2$), carbon monoxide (CO), forms formic acid (H_2CO_2) with water ($H_2O + CO = H_2CO_2$). Sulphur dioxide or sulphurous anhydride (SO_2) produces sulphurous acid (H_2SO_3) with water ($H_2O + SO_2 = H_2SO_3$). This is known from its salts as sodium sulphite (Na_2SO_3) or the acid sulphite ($NaHSO_3$). Phosphorus trioxide (P_2O_3) produces phosphorous acid (H_3PO_3) with water ($3H_2O + P_2O_3 = 2H_3PO_3$). The salts of these acids are however not found in nature and therefore they need not be further considered.

The three compounds, hydrogen chloride (HCl), hydrogen bromide (HBr) and hydrogen sulphide (H_2S) are gases under ordinary conditions, and acquire acid properties only when dissolved in water. Of these HCl and HBr most readily combine with water, the gases being seldom found in a free state. H_2S, however, is commonly a gas; when dissolved in water it forms a weak acid. Its salts are sulphides and they are abundantly represented in nature by the sulphides of the metals. The salts of hydrochloric acid (HCl) are chlorides, such as sodium chloride or common salt; the salts of hydrobromic acid (HBr) are bromides.

The salts of the other acids in the list are called nitrates, carbonates, sulphates, phosphates, borates and silicates.

When an acid has an atom of hydrogen (HCl)[1] or one hydroxyl radical (HNO_3) it is called a monobasic acid and will form only one type of salt with a hydroxide such as NaOH (*i.e.*, NaCl; $NaNO_3$); when two hydrogen atoms or two hydroxyl radicals are present the acid is dibasic (H_2S; H_2CO_3) and two salts, an acid and a normal one may be formed (NaHS and Na_2S; $NaHCO_3$ and Na_2CO_3); when the acid contains three hydroxyl radicals, three salts, two acid and a normal one may be formed (Ex. NaH_2PO_4, Na_2HPO_4 and Na_3PO_4). One of the phosphoric and two of the silicic acids are tetrabasic.

Bases.—This term is applied to a hydroxide, or the combinations of positive elements such as potassium, sodium, calcium, iron, etc., with a hydroxyl radical (OH) as Na(OH) or a combination of a positive radical with the hydroxyl radical as in $NH_4(OH)$. It may also be considered as formed by the oxide of such elements with water as $Na_2O + H_2O = 2Na(OH)$. Again, it may be formed by the combination of a basic radical with a hydroxyl radical, as in (AlO) (OH) or (FeO) (OH), in other words, by an oxyhydroxide.

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[1] Owing to its usual occurrence in solution only the symbol of hydrogen chloride (HCl) is generally used for that of hydrochloric acid as well, instead of HCl + Aq.

Among the common bases which enter into the formation of the salts discussed in this book are:

$NH_4(OH)$	Ammonium hydroxide	$(OH) - NH_4$
$K(OH)$	Potassium hydroxide	$(OH) - K$
$Na(OH)$	Sodium hydroxide	$(OH) - Na$
$Ca(OH)_2$	Calcium hydroxide	$(OH)_2 = Ca$
$Mg(OH)_2$	Magnesium hydroxide	$(OH)_2 = Mg$
$Ba(OH)_2$	Barium hydroxide	$(OH)_2 = Ba$
$Sr(OH)_2$	Strontium hydroxide	$(OH)_2 = Sr$
$Fe(OH)_2$	Ferrous hydroxide	$(OH)_2 = Fe''$
$Fe(OH)_3$	Ferric hydroxide	$(OH)_3 \equiv Fe'''$
$Al(OH)_3$	Aluminum hydroxide	$(OH)_3 \equiv Al$
$Cu(OH)$	Cuprous hydroxide	$(OH) - Cu$
$Cu(OH)_2$	Cupric hydroxide	$(OH)_2 = Cu$

A base is called monacidic if one hydroxyl group can be replaced (KOH, NaOH), diacidic if two hydroxyl groups can be replaced ($Ca(OH)_2$, $Mg(OH)_2$), triacidic if three hydroxyl groups can be replaced ($Fe'''(OH)_3$; $Al(OH)_3$) and so forth.

In the formation of a salt the hydroxyl group or (OH) radical is replaced by the acid, and joins with the hydrogen of that acid to form water thus:

$$\begin{aligned} NaOH &+ HCl &= NaCl &+ H_2O \\ Ca(OH)_2 &+ H_2SO_4 &= CaSO_4 &+ 2H_2O \end{aligned}$$

Salts.—We may now define a salt more precisely as the compound formed by the reaction between an acid and a base, or the product of the replacement of one or more hydrogen atoms of an acid by a positive element or basic radical, or the product of the replacement of one or more hydroxyl radicals of a base by a negative element or acid radical. Thus the common salt sodium chloride NaCl may be considered as produced from hydrochloric acid HCl and the base sodium hydroxide (NaOH) by the replacement of the hydrogen of the acid HCl, with the sodium of the base NaOH, or it may be regarded as formed by the replacement of the hydroxyl radical OH of the base NaOH, with the negative element chlorine of the acid HCl. In either case, the replaced and discarded parts, *i.e.*, the H and the OH, combine to form water. The reaction is $NaOH + HCl = NaCl + H_2O$. There is of course no actual formation of salt until evaporation takes place, the Na and Cl remaining in the ionized state in the solution.

Again, the salt calcium sulphate ($CaSO_4$) may be considered as formed by the replacement in the acid H_2SO_4 of the two hydrogen atoms by the bivalent calcium atom of the hydroxyl or base $Ca(OH)_2$ or by the replacement of the two hydroxyls of the base by the SO_4 radical of the acid. As before, the freed hydrogen and hydroxyls combine to form water. The reaction is:

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

New salts may also be formed by the reaction in solution of a strong acid upon a salt with a weak acid, especially if the new salt is less soluble than the older one. Thus, if dilute sulphuric acid is added to a solution of strontium chloride, the less soluble salt strontium sulphate is formed. The reaction is:

$$SrCl_2 + H_2SO_4 = SrSO_4 + 2HCl.$$

Again two new salts may be formed by the recombination of the ions of two salts in a solution if one of the new salts is less soluble. Thus barium chloride and sodium sulphate will react to form the insoluble salt barium sulphate and the soluble salt sodium chloride. The reaction is:

$$BaCl_2 + Na_2SO_4 = \downarrow BaSO_4 + 2NaCl.$$

The new salt thus formed in both cases cited is precipitated out. To such salts the term *precipitated salt* or *precipitate* is applied.

As the salts in solution are considered to be in an ionic state, evaporation of the solution results in the recombining of the separated ions provided no new exchange or reaction takes place. As a result the same salts which have been dissolved are found again as the solution is condensed. Such salts are called *evaporated salts*, or *evaporates*. Sodium chloride formed from ocean water is an illustration. It can, of course, not be denied, that the salts obtained from ocean water on evaporation may be in part salts which have formed as the result of the recombination of the ions of other salts brought originally into the sea. Practically then we must restrict the term precipitate to the insoluble or less soluble salt which is formed as the result of such a reaction, while the other salt which remains in solution until evaporation takes place is classed as an evaporate. Thus in the above reaction between $BaCl_2$ and Na_2SO_4 the resulting insoluble $BaSO_4$

is the precipitate, while the NaCl which is formed will not solidify until the proper amount of evaporation of the water has been accomplished. It then becomes an evaporation salt or an evaporate. The value of this distinction will become more obvious when we consider the deposits made in the sea.

Salts may be classified as (1) simple or normal (also called neutral), (2) compound, and (3) complex or double and triple.

Normal Salts.—These are salts in which all the hydrogen elements of the acid have been replaced by a base, as NaCl, Na_2CO_3, etc.

Compound Salts.—These comprise several types.

1. *Acid Salts.*—These are salts in which only part of the hydrogen has been replaced by a positive substance, one or more of the hydrogen atoms still remaining as in $NaHCO_3$, the acid carbonate of sodium which occurs in nature forming with the normal carbonate and water the mineral trona ($Na_2CO_3.NaHCO_3.2H_2O$). Two acid salts besides the normal may be formed from tribasic acids. Thus from the orthophosphoric acid, H_3PO_4 we may derive with the base NaOH, two acid salts, (1. Sodium di-hydrogen phosphate, NaH_2PO_4, primary phosphate. 2. Sodium hydrogen phosphate, Na_2HPO_4, secondary phosphate), and a normal salt, (3. tri-sodium phosphate, Na_3PO_4, tertiary phosphate).

2. *Basic Salts.*—These are salts in which part of the basic hydroxyl remains as in Ca(OH)Cl, the normal salt of which is $CaCl_2$. Again, two basic salts may be derived from a triacidic base as the hydroxide of bismuth ($Bi(OH)_3$), the normal nitrate of which is $Bi(NO_3)_3$. These basic salts are $Bi(OH)_2NO_3$ and $BiOH(NO_3)_2$.

3. *Mixed Salts.*[1]—These are salts in which the hydrogen radicals of the acids have been replaced by two (or more) different positive elements as in the sodium potassium carbonate $(NaK)CO_3$, $\left.\begin{matrix}Na-\\K-\end{matrix}\right\}CO_3$, and in dolomite $(CaMg)CO_3$, $\left.\begin{matrix}Ca-\\Mg-\end{matrix}\right\}CO_3$, when this is not regarded as a double salt.

Complex Salts.—These include the following:

4. *Double Salts.*—These are combinations of two distinct salts into an isomorphous compound, as ordinary alum or potassium-aluminum sulphate (K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$), which is an isomorphous compound of potassium sulphate and aluminum

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[1] The name "mixed salts" has also been applied to acid and basic salts, but is here used in the restricted sense.

sulphate with 24 molecules of water (see under hydration). The mineral Schönite found at Stassfurt is the double sulphate of magnesium and potassium with 6 molecules of water ($MgSO_4$, K_2SO_4, $6H_2O$). The mineral trona mentioned above is the isomorphous compound of the normal and acid carbonates of sodium with two molecules of water. Many double salts are known in the natural salt deposits and will be referred to again later.

Generally, double salts have the same acid radical while the basic radicals are different. There are some, however, with the same basic but different acid radicals. An example of this is the mineral Darapskite, which is the nitrate and sulphate of sodium with one molecule of water ($NaNO_3$, Na_2SO_4, H_2O). Finally there are double salts in which both acid and basic radicals are different, as in the mineral Kainite, an important potash salt of Stassfurt which is the compound of sulphate of magnesium and chloride of potassium with three molecules of water ($MgSO_4$, KCl, $3H_2O$).

5. *Triple Salts.*—These are also known in nature. One of the most important at Stassfurt is Polyhalite, the triple sulphate of calcium, magnesium and potassium with two molecules of water ($2CaSO_4$, $MgSO_4$, K_2SO_4, $2H_2O$). The mineral Krugite, a triple sulphate of the same bases differs from this in having twice the amount of $CaSO_4$ found in Polyhalite. The formula for Krugite is $4CaSO_4$, $MgSO_4$, K_2SO_4, $2H_2O$. The salt Hanksite is a still more complex one, consisting apparently of the sulphate and carbonate of sodium and the chloride of potassium with the following formula: $9Na_2SO_4$, $2Na_2CO_3$, KCl. It has thus two different basic and three different acid radicals, which is expressed in writing the formula as follows:

$$Na_{22}K(SO_4)_9(CO_3)_2Cl.$$

Double salts are very common among the silicates and triple and even more complex salts are known. With these, however, we have no concern in this book.

HYDRATION AND HYDRATES

The combination of oxides with water produces hydroxides or oxyhydroxides with the separation of water. Many salts will, however, combine with water directly to form a hydrous salt, and to such the name *hydrate* is applied. If a molecule of a salt combines with one of water it is a monohydrate like the mineral Kieserite ($MgSO_4.H_2O$). If two molecules of water are taken up, a dihydrate is produced, *i.e.*, gypsum ($CaSO_4.2H_2O$). The mineral Kainite is a tri-hydrate ($KCl.MgSO_4.3H_2O$) and the mineral Astrakanite a tetrahydrate ($Na_2SO_4.MgSO_4.4H_2O$).

Blue vitriol is a pentahydrate ($CuSO_4. 5H_2O$), Bischofite a hexahydrate ($MgCl_2.6H_2O$) and Reichardtite a heptahydrate ($MgSO_4.7H_2O$). Decahydrates, in which ten molecules of water are taken up are not uncommon, as in the case of the mineral Natron (or the common chemical product known as washing soda) $Na_2CO_3.10H_2O$ and the mineral Mirabilite (or Glauber salt) $Na_2SO_4.10H_2O$. When no water is present in the salt, it is said to be anhydrous, or an anhydrate. Common anhydrates are:

Anhydrite	$CaSO_4$	Calcite	$CaCO_3$
Thenardite	Na_2SO_4	Halite	$NaCl$
Soda Niter	$NaNO_3$	Sylvite	KCl

Hemi-hydrates are also known, such as the common product of burned gypsum, *i.e.*, plaster of Paris, which has the reaction formula $CaSO_4.\frac{1}{2}H_2O$.

Hydrates of a higher denomination may sometimes be reduced to one of lower by the influence of a dehydrating substance or by heat. Thus in the presence of magnesium chloride ($MgCl_2$) which is a dehydrating agent, the heptahydrate $MgSO_4.7H_2O$ (Reichardtite) will lose one molecule of water and become the hexahydrate $MgSO_4. 6H_2O$. This substance does not, however, exist in nature in solid form. Some hydrates are unstable in air, and lose part or all of their water of hydration, a process called *efflorescence*. Such is the case with Glauber salt (Mirabilite) $Na_2SO_4. 10H_2O$ which on exposure to air loses all of its water and becomes the anhydrate Na_2SO_4 (Thenardite). This is due to the fact that the decahydrate has a greater aqueous tension than 5 mm. at 1°C., which is the average vapor pressure of water in the atmosphere. When, on the other hand, a hydrate has a lower vapor tension, it will often take on water from the air, and become moist and dissolve in the water. This behavior is called *deliquescence*, and the salt is said to be *hygroscopic*. Thus the dihydrate of calcium chloride $CaCl_2. 2H_2O$ will take water from the air or from many substances to form the hexahydrate $CaCl_2. 6H_2O$. It is therefore commonly used as a drying agent. The

$MgCl_2$ in common salt causes it to become damp by absorbing water from the air.

Even nearly pure sodium chloride (common salt) is hygroscopic, as soon as the relative humidity (see p. 113) of the air exceeds 72 per cent. at a temperature of 25° to 30°C. (77° to 86°F.), a fact familiar to many a housewife. Below these humidity and temperature limits, however, pure salt (NaCl) even when wet, will give off its water to the air. The sea-salt made on the island of Java, however, is so impure, that it obstinately retains from 5 to 6 per cent. of water, on which account it will deliquesce whenever the relative humidity rises above 64 per cent. As the relative humidity of that island is over 80 per cent. (in 1891 at Batavia it was 83.3 per cent. with a mean annual temperature of 25.78° to 26°C.) it has been found exceedingly difficult to keep this salt, and it has to be placed in dry storage for 3 or 4 years after manufacture before it can be used. To make exportation of such salt possible, centrifugal drying and compression into briquettes is resorted to, a pressure of 200 atmospheres being required to free it from all mother-liquor, and this is accompanied by a diminution in volume of one-half. These briquettes are packed in moisture-proof paper.

WATER OF CRYSTALLIZATION

The term *water of crystallization* is often used to designate the water taken up by hygroscopic mineral substances. Since, however, such substances are not always crystalline and since, moreover, many crystallized substances are without water (anhydrates) the term is objectionable. Such water is properly called *water of hydration.*

SOLUTIONS[1]

The term solution in its widest sense implies the mingling of two or more substances in such a way that a homogeneous substance is produced in which the separate components can not be distinguished, except by test. While ordinarily a solution is the result of the dissolving of a solid in a liquid, solutions of liquids in liquids (alcohol in water) and gases in liquids (air in water) are also possible. Likewise solutions of gases, liquids and even solids in other solids are known.

In our studies, when the term solution is used, we refer to the commonest type, namely, the solution of a solid in water. This must be carefully distinguished from *suspension* of a substance in water, a condition which obtains when the solid exists in finely divided but visible particles in the water, and will usually settle out after a time. Even when the substance is so finely divided that it will not be retained by filter paper, it still forms a *colloidal suspension*, and the liquid is cloudy, opalescent or opaque. Liquids, too, may be suspended in minute drops in other liquids forming an *emulsion*. A solution is characterized by an apparently complete dispersion of the dissolved substance in the liquid so that the latter appears clear, transparent and perfectly homogeneous, and the solution can not be distinguished from the pure liquid by the eye unless coloration is produced. The liquid which, like water, forms the bulk of the solution, is the *solvent*. The substance dissolved in it is the *solute*. The actual amount of a substance dissolved in a given quantity of the solvent determines the concentration of the solution. Small quantities of a solute in the solvent make the solution weak or *dilute*. Large quantities make the solution strong or *concentrated*. When the solution contains all of the solute, which it can hold at a given temperature under normal conditions it is called *saturated*, but this will vary with the temperature of the solvent and solute, the solubility of the solute generally rising with increase in temperature of either or both, though in a few cases it decreases. For example, 100 grams of water, which will hold 13 grams of potassium nitrate at 0°C., will dissolve 150 grams at 73°C., thus indicating an enormous increase in power of solution. For sodium chloride (common salt) the increase is very slight; 100 grams of water will dissolve 35.6 grams of NaCl at 0°C. and only 39 grams at 100°C. On the other hand, a decreasing solubility with increase of temperature is seen in calcium hydroxide $Ca(OH)_2$ (slaked lime) which is 0.175 gram in 100 grams of water at 20° and 0.078 gram at 100°C.

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[1] H. C. Jones, The Nature of Solutions, Van Nostrand, 1917.

A saturated solution in water, at a given temperature, is produced by adding an excess of the solute, so that after prolonged stirring some of it still remains on the bottom of the vessel (the "Bodenkörper" of van't Hoff). It should here be noted that a solution may become saturated without reference to its degree of concentration, for a substance of low solubility may form a saturated solution which is very dilute. Thus 100 cc. of water are saturated at 180° with 0.0013 gram of $CaCO_3$ yet the solution is very dilute. The same amount of water, however, will take up 200 grams of calcium iodide before saturation is reached, thus making a very concentrated solution. The degree of concentration of a solution, saturated or otherwise, is often given in *physical units* which implies the number of grams of the solute held in solution by 100 grams of the solvent. (In the case of a solvent of pure water 100 cc.) The degree of concentration may also be expressed in equivalent weights of the substance. A solution which contains 1 gram-equivalent of the solute, in 1 liter of the solution (not 1 liter of the solvent) is called a *normal solution*. An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element. The equivalent weight for HCl is 36.5 grams containing 1 gram of H; for H_2SO_4, ½ of 98; for $AlCl_3$, ⅓ of 133.5. Thus a normal solution of HCl contains 36.5 grams; of H_2SO_4, 49 grams, and of $AlCl_3$, 44.5 grams per liter of the solution.

When more than one salt is dissolved in a given solvent, the degree of concentration is called the salinity of the solution, and is commonly expressed in grams per liter of the solution (not in a liter of the solvent). This is called the *permillage* (see further under Chapter III, Salinity of the Sea, etc.).

The excess of material will have no influence in changing the amount dissolved in the water at that temperature, once the solution has become saturated. The substances are in equilibrium, though an interchange of molecules between the solid and the solution may still go on, the equilibrium being maintained by simultaneous solution in one and deposition in another place.

In the following table from Alexander Smith's Chemistry, the solutions of 142 bases and anhydrous salts are given in grams per 100 cc. of water at the temperature of 18°C. (64.4°F.).[1] The solution experiments of Van't Hoff and his associates to be cited in Chapter III were made at the laboratory temperature of 23°C. (73.4°F.).

These numbers give the number of grams of the anhydrous salt held in solution by 100 cc. of water. Numbers for small solubility have been abbreviated; thus 0.0_316 signifies 0.00016, etc.

A super-saturated solution is one that contains more of the solute at a given temperature than it would take up at that

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[1] General Chemistry for Colleges. Alexander Smith, 1916, Century Co. Preface.

TABLE III.—SOLUBILITY TABLES

A. Solubilities of Bases and Salts in Water at 18 C.

	K	Na	Li	Ag	Ti	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32.95	35.86	77.79	$0.0_{3}16$	0.3	37.24	51.09	73.19	55.81	203.9	1.49
Br	65.86	88.76	168.7	$0.0_{4}1$	0.04	103.6	96.52	143.3	103.1	478.2	0.598
I	137.5	177.9	161.5	$0.0_{6}35$	0.006	201.4	169.2	200.0	148.2	419.0	0.08
F	92.56	4.44	0.27	195.4	72.05	0.16	0.012	0.0016	0.0076	0.005	0.07
NO_3	30.34	83.97	71.43	213.4	8.91	8.74	66.27	121.8	74.31	117.8	51.66
ClO_3	6.6	97.16	313.4	12.25	3.69	35.42	174.9	179.3	126.4	183.9	150.6
BrO_3	6.38	36.67	152.5	0.59	0.30	0.8	30.0	85.17	42.86	58.43	1.3
IO_3	7.62	8.33	80.43	0.004	0.059	0.05	0.25	0.25	6.87	0.83	0.002
OH	142.9	116.4	12.04	0.01	40.04	3.7	0.77	0.17	0.001	$0.0_{3}5$	0.01
SO_4	11.11	16.83	35.64	0.55	4.74	$0.0_{3}23$	0.011	0.20	35.43	53.12	0.0041
CrO_4	63.1	61.21	111.6	0.0025	0.006	$0.0_{3}38$	0.12	0.4	73.0	....	$0.0_{4}2$
C_2O_4	30.27	3.34	7.22	0.0035	1.48	0.0086	0.0046	$0.0_{3}56$	0.03	$0.0_{3}6$	$0.0_{3}15$
CO_3	108.0	19.39	1.3	0.003	4.95	0.0023	0.0011	0.0013	0.1	0.004?	$0.0_{3}1$

B. Solubility of Some Common Salts[1]

Salt	Temperature, ° C.	Amount of pure compound without water of crystallisation	
		Dissolved in 100 grams of water, grams	Dissolved in 100 cubic centimeters of the solution, grams
Sodium chloride (Na.Cl)	0	35.7	
Sodium chloride (Na.Cl)	10	35.8	
Sodium chloride (Na.Cl)	25	36.12	
Sodium chloride (Na.Cl)	50	37.0	
Sodium chloride (Na.Cl)	100	39.8	
Sodium sulphate ($Na_2SO_4.10H_2O$)	0	5.0	
Sodium sulphate ($Na_2SO_4.10H_2O$)	25	28.0	
Sodium sulphate ($Na_2SO_4.7H_2O$)	0	19.5	
Sodium sulphate ($Na_2SO_4.7H_2O$)	25	53.0	
Sodium bromide (Na.Br)	0	66.0	
Sodium bromide (Na.Br)	20	77.0	
Sodium iodide ($NaI.2H_2O$)	0	158.7	
Sodium iodide ($NaI.2H_2O$)	25	184.2	
Potassium chloride (KCl)	0	27.6	
Potassium chloride (KCl)	25	35.5	
Potassium sulphate (K_2SO_4)	0	7.35	
Potassium sulphate (K_2SO_4)	25	10.75	
Potassium bromide (KBr)	0	53.5	
Potassium bromide (KBr)	25	67.7	
Potassium iodide (KI)	0	127.5	
Potassium iodide (KI)	25	148.0	
Calcium chloride ($CaCl_2.6H_2O$)	0	59.5	
Calcium chloride ($CaCl_2.6H_2O$)	20	91.0	
Calcium sulphate ($CaSO_4.2H_2O$)	0	....	0.1759
Calcium sulphate ($CaSO_4.2H_2O$)	25	....	0.2080
Calcium sulphate ($CaSO_4.2H_2O$)	25	....	0.426[2]
Calcium sulphate ($CaSO_4.2H_2O$)	25	....	0.569[3]
Calcium sulphate ($CaSO_4.2H_2O$)	25	....	0.1620[4]
Calcium sulphate ($CaSO_4.2H_2O$)	25	....	0.1471[5]
Calcium sulphate ($CaSO_4.2H_2O$)	26	....	0.666[6]
Calcium sulphate ($CaSO_4.2H_2O$)	26	....	0.650[7]
Magnesium sulphate ($MgSO_4.7H_2O$)	0	26.9	
Magnesium sulphate ($MgSO_4.7H_2O$)	25	38.5	
Magnesium chloride ($MgCl_2.6H_2O$)	0	52.8	
Magnesium chloride ($MgCl_2.6H_2O$)	25	56.7	
Magnesium bromide ($MgBr_2.6H_2O$)	0	91.9	
Magnesium bromide ($MgBr_2.6H_2O$)	25	97.6	
Magnesium iodide ($MgI_2.8H_2O$)	25	....	54.4[8]

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[1] Seidell, Atherton, "Handbook of Solubilities," New York, 1907. (Quoted by Phalen, W. C., Salt Resources of the United States. United States Geological Survey, *Bulletin* 669, p. 196, 1919.)

[2] Solution containing 8.5 grams per liter of $MgCl_2$.

[3] Solution containing 19.8 grams per liter of $MgCl_2$.

[4] Solution containing 3.20 grams per liter of $MgSO_4$.

[5] Solution containing 10.64 grams per liter of $MgSO_4$.

[6] Solution containing 91.15 grams per liter of NaCl.

[7] Solution containing 264.17 grams per liter of NaCl.

[8] Dissolved in 100 grams of the aqueous solution.

temperature from stirring with the undissolved solute. It may be produced by cooling a saturated solution after removal of all the undissolved bottom substances. Thus if 100 cc. of water are saturated with Glauber salt ($Na_2SO_4.10H_2O$) at 30° it will take up 40 grams of the solute. After removal of the bottom salt the solution may be cooled to 15° at which temperature the water would take up only 13 grams of the salt. The excess of 27 grams will, however, remain in solution until the introduction of a crystal, however minute, of the Glauber salt, when crystallization will at once begin around it.

Solutions of any degree short of saturation are *concentrated* by the partial removal of the solvent, as by evaporation of a salt in water. By this process a state of saturation is reached for the given temperature, beyond which further evaporation will result in the separation out of the salt. This separation of the salt is complete when the solution is *evaporated* to dryness, and the salt remains behind as the *residue*. The salt (or other substance) separated out during concentration, as well as the final residue, may be spoken of as the *evaporate*.

Changes in Volume on Solution[1]

A remarkable and still unexplained phenomenon accompanies the solution of many salts in water, namely, the change in volume disproportional to that required by the volumes of the solvent and solute. Thus, when 250 gr. of NaCl, which occupies a volume of 116 cc. is dissolved in one liter of water (1,000 cc.) the volume of the solution is only 1,086 cc. instead of 1,116, the sum of the two volumes. There is thus a shrinkage in volume of 30 cc. during the process of the solution. When, however, 214 gr. of ammonium chloride, which has a volume of 142.5 cc., is dissolved in 843.5 cc. of water, 1,000 cc. of the solution results, although the combined volume of the salt and water makes only 986 cc. Here, then, there is an expansion of 14 cc. during the process of solution.

CLASSIFICATION OF THE NATURAL SALTS AND SALT-LIKE SUBSTANCES

The usual, and in many respects most satisfactory method of classifying salts is by their negative or acid elements, giving us chlorides, sulphates, carbonates, etc. Under each of these groups the salts may most conveniently be arranged in the order of their complexity, normal salts being placed first, followed by acid, basic, mixed, double and finally triple salts if such occur. Each of these groups may again be divided, according to the degree of hydration.

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[1] A. Smith's Chemistry.

As stated at the opening of this chapter, certain oxides, hydroxides and oxyhydroxides will be included with the salts in this treatise, on account of their importance to the salt geologist. These will precede the salts in the classification. Where free acids occur in nature they are placed at the head of the salts formed by them. The following lists contain only the more important salts.

I. **Native elements:**
  - Sulphur (S).
  - Carbon, Diamond, Graphite, etc. (C).

II. **Oxides:** Of the many oxides the following are included:
  - Silica (quartz, etc.) (SiO_2).
  - Opal ($SiO_2 + nH_2O$).
  - Corundum (Al_2O_3).
  - Water, ice (H_2O).
  - Hausmannite (Mn_3O_4).
  - Manganite ($Mn_2O_3.H_2O$).
  - Periclase (MgO).
  - Rutile (TiO_2).
  - Spinel ($MgO.Al_2O_3$).
  - Chrysoberyl ($BeO.Al_2O_3 + Fe$).

III. **Hydroxides:** Of these the following are included:
  - Hydrargillite (Gibbsite) ($Al(OH)_3$).
  - Brucite ($Mg(OH)_2$).

IV. **Oxyhydroxides:** This class includes:
  - Diaspore (AlO(OH)) etc., and among the metallic compounds.
  - Goethite (FeO(OH)).
  - Limonite ($Fe_4O_3(OH)_6$), and others.

V. **Chlorides:**
  - *A. Simple salts:*
    - Sylvite (KCl).
    - Halite (NaCl).
    - Salmiak (NH_4Cl).
    - Bischofite ($MgCl_2.6H_2O$).
    - Chlorocalcite ($CaCl_2$).
  - *B. Double salts:*
    - Baeumlerite ($CaCl_2.KCl$).
    - Douglasite ($2KCl.FeCl_2.2H_2O$).
    - Carnallite ($KCl.MgCl_2.6H_2O$).
    - Tachhydrite ($2MgCl_2, CaCl_2.12H_2O$).

- *C. Triple salts:*
  - Koenenite ($Al_2O_3.3(MgO).2(MgCl_2).6$ or $8H_2O$ empirical formula).
  - Kremersite ($K(NH_4)FeCl_5.H_2O$).
  - Rinneite ($FeCl_2.3KCl.NaCl$).

VI. Sulphato-chlorides: 1
- Kainite ($KCl, MgSO_4, 3H_2O$).
- Sulphohalite ($2NaCl.2Na_2SO_4$).
- Chlorothionite ($K_2SO_4.CuCl_2$).

VII. Bromides: Found in natural waters probably as sodium and potassium bromides.

VIII. Iodides (omitted).

IX. Fluorides:
- Fluorite (CaF_2).
- Sulphohalite ($NaF.NaCl. 2Na_2SO_4$ or $2NaCl.2Na_2SO_4$).
- Cryolite (Na_3AlF_6).
- Hieratite (K_2SiF_6).

X. Sulphide:
- Iron Pyrites (FeS_2).

XI. Nitrates and Sulphato-nitrates:
- Bengal saltpeter or potash niter KNO_3.
- Chile saltpeter or soda niter ($NaNO_3$).
- Nitrobarite ($Ba(NO_3)_2$).
- Nitrocalcite ($Ca(NO_3)_2$).
- Nitromagnesite ($Mg(NO_3)_2nH_2O$).
- Gerhardtite ($Cu_4(OH)_6.(NO_3)_2$).
- Darapskite ($NaNO_3.Na_2SO_4.H_2O$).
- Nitroglauberite ($6NaNO_3.2Na_2SO_4.3H_2O$).

XII. Chlorates (omitted).

XIII. Bromates (omitted).

XIV. Iodates:
- Lautarite (CaI_2O_6).
- Dietzeite ($7CaI_2O_6.8CaCrO_4$).

XV. Sulphates:
- *A. Simple salts:*
  - Thenardite (Na_2SO_4).
  - Mirabilite ($Na_2SO_4.10H_2O$).
  - Barite ($BaSO_4$).
  - Celestite ($SrSO_4$).
  - Anhydrite ($CaSO_4$).
  - Gypsum ($CaSO_4.2H_2O$).
  - Kieserite ($MgSO_4.H_2O$).
  - Reichardtite (Epsomite) ($MgSO_4.7H_2O$).
  - Alunogen ($Al_2(SO_4)_3.18H_2O$).
- *B. Double salts:*
  - Glaserite ($KNaSO_4$ to $K_3Na(SO_4)_2$).
  - Syngenite ($CaSO_4.K_2SO_4.H_2O$).
  - Langbeinite ($2MgSO_4.K_2SO_4$).
  - Leonite ($MgSO_4.K_2SO_4.4H_2O$).

Schönite ($MgSO_4.K_2SO_4.6H_2O$).

Vanthoffite ($MgSO_4.3Na_2SO_4$).

Loeweite ($MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$).

Bloedite or Astrakanite ($MgSO_4.Na_2SO_4.4H_2O$).

Glauberite ($CaSO_4.Na_2SO_4$).

Boussingaultite ($(NH_4)_2SO_4.MgSO_4.6H_2O$).

Pickeringite ($MgSO_4.Al_2(SO_4)_3.22H_2O$).

Loewigite ($K_2O.3Al_2O_3.4SO_3.9H_2O$).

Alunite ($K(AlO_2H_2)_3(SO_4)_2$ or, $K_2O.3Al_2O_3.4SO_4.6H_2O$)

Kalinite ($KAl(SO_4)_2.12H_2O$).

Mendozite ($NaAl(SO_4)_2.12H_2O$).

Tschermigite ($(NH_4)Al(SO_4)_2.12H_2O$).

Halotrichite ($FeSO_4.Al_2(SO_4)_3.24H_2O$).

Cyanochroite ($K_2SO_4.CuSO_4.6H_2O$).

C. Triple salts:

Polyhalite ($2CaSO_4.MgSO_4.K_2SO_4.2H_2O$).

Krugite ($K_2SO_4.4CaSO_4.MgSO_4.2H_2O$).

Natroalunite ($K.Na(AlO_2H_2)_3(SO_4)_2$).

Plagiocitrite ($KNa(Fe(OH)_2)_3(SO_4)_2$).

XVI. Chromate:

Dietzeite ($8CaCrO_4.7CaI_2O_6$).

XVII. Carbonates:

A. Simple salts:

Soda (Na_2CO_3).

Acid carbonate ($NaHCO_3$).

Thermonatrite ($Na_2CO_3.H_2O$).

Natron ($Na_2CO_3.10\ H_2O$).

Calcite, Aragonite, Ktypeite ($CaCO_3$).

Magnesite ($MgCO_3$).

Strontianite ($SrCO_3$).

Witherite ($BaCO_3$).

Smithsonite ($ZnCO_3$).

Siderite ($FeCO_3$).

B. Double salts:

Dolomite ($(CaMg)CO_3$) or ($CaCO_3.MgCO_3$).

Trona (Urao) ($Na_2CO_3.NaHCO_3.2H_2O$).

Pierssonite ($Na_2CO_3.CaCO_3.2H_2O$).

Gaylussite ($Na_2CO_3.CaCO_3.5H_2O$).

XVIII. Chloro-carbonate:

Northrupite ($Na_2CO_3.MgCO_3.NaCl$) (Triple salt).

XIX. Sulpho-carbonate:

Tychite ($2(Na_2CO_3).2(MgCO_3).Na_2SO_4$) (Triple salt).

XX. Sulpho-chloro-carbonate:

Hanksite ($KCl.2Na_2CO_3.9Na_2SO_4$) (Triple salt).

XXI. Boric acid and borates:

A. Orthoboric acid:

Sassolite (H_3BO_3).

B. Simple salts:

Larderellite ($(NH_4)_2B_8O_{13}.4H_2O$).

Borax ($Na_2B_4O_7.10H_2O$).
Pinnoite ($MgB_2O_4.3H_2O$).
Ascharite ($3Mg_2B_2O_5.2H_2O$).
Bechilite or borocalcite ($CaB_4O_7.4H_2O$).
Hayesine ($CaO_2.2B_2O_3.6H_2O$).
Priceite ($3CaO.4B_2O_3.6H_2O$).
Colemanite ($Ca_2B_6O_{11}.5H_2O$).
Pandermite ($Ca_3B_{20}O_{18}.15H_2O$).
Lagonite ($Fe_2O_3.3B_2O_3.3H_2O$).

C. Double salts:

Hydroboracite ($CaMgB_6O_{11}.6H_2O$).
Ulexite ($NaCaB_5O_9.8H_2O$).
Heintzite ($KMg_2B_{11}O_{19}.7H_2O$).

XXII. Chloro-borates:

Boracite ($Mg_7B_{16}O_{30}Cl_2$). or ($MgCl_2.2Mg_3B_8O_{15}$).

XXIII. Sulpho-borate:

Sulphoborite ($2MgSO_4$ $4MgHBO_3.7H_2O$).

XXIV. Borosilicates:

Searlesite ($Na_2O.B_2O_3.4SiO_2.2H_2O$).
Bakerite ($8CaO.5B_2O_3.6SiO_2.6H_2O$).

XXV. Phosphates:

A. Simple salts:

Monetite ($HCaPO_4$).
Brushite ($HCaPO_4.2H_2O$).
Metabrushite ($2HCaPO_4.3H_2O$).
Martinite ($2H_2Ca_5(PO_4)_4.H_2O$).
Collophanite ($Ca_3P_2O_8.H_2O$).
Bobierrite ($Mg_3P_2O_8.8H_2O$).
Newberyite ($HMgPO_4.3H_2O$).
Vivianite ($Fe_3P_2O_8.8H_2O$).
Turquois ($2Al_2O_3.P_2O_5.5H_2O$).
Variscite ($Al_2O_3.P_2O_5.4H_2O$).
Wardite ($2Al_2O_3.P_2O_5.7H_2O$).
Minervite ($H_2KAl_2(PO_4)_3.6H_2O$)

B. Double salts:

Hannayite ($Mg_3P_2O_8.2H_2(NH_4)PO_4.8H_2O$).
Struvite ($(NH_4)MgPO_4.6H_2O$).
Stercorite ($HNa(NH_4)PO_4.4H_2O$).
Barrandite ($(Al.Fe)PO_4.2H_2O$).

C. Triple salts:

Lazulite ($2Al(OH).MgPO_4.FePO_4$).

XXVI. Fluor- and Chloro-phosphates:

Fluorapatite ($Ca_5(PO_4)_3.F$).
Chlorapatite ($Ca_5(PO_4)_3.Cl$).

XXVII. Phosphato-carbonate:

Dahllite ($2Ca_3P_2O_8.CaCO_3.\frac{1}{2}H_2O$).

XXVIII. Phosphato-silicate:

Ciplyte ($4CaO.2P_2O_5.SiO_2$?).

XXIX. Silicates. The numerous silicates found in nature are omitted in this book except the following:
- Kaolinite ($H_4Al_2.Si_2O_9$).
- Nontronite ($H_4Fe_2Si_2O_9$).

XXX. Hydrocarbons: general formula; (C_nH_{2n}).
- Amber.
- Asphaltum.
- Dysodile.
- Jet.
- Ozokerite.
- Pyropissite.
- Petroleum (C_nH_{2n+2}).

CHAPTER II

MINERAL CHARACTERS AND OCCURRENCE OF THE MORE IMPORTANT NON-METALLIC SALTS OTHER THAN SILICATES AND THE IMPORTANT OXIDES, HYDROXIDES, HYDROCARBONS AND NON-METALLIC NATIVE ELEMENTS WHICH OCCUR IN MINERAL FORM IN NATURE IN ALPHABETICAL ARRANGEMENT[1]

Acid Carbonate of Soda.—See **Trona.**

Agate.—Banded cryptocrystalline quartz.

Alabaster.—See **Gypsum.**

Alunite.—$K(AlO_2H_2)_3(SO_4)_2$ or $K_2O.3Al_2O_3.4SO_3.6H_2O$; sp. gr.: 2.6–2.75 and 2.82; H: 3.5–4; colorless to yellowish; insoluble; as crystals: in carnallite, in altered igneous rocks and in veins; Occ.: Utah, Col., Nev., Cal., Ariz., Italy, N. S. Wales, etc.

Alunogen.—$Al_2(SO_4)_3.18H_2O$; monoclinic; sp. gr.: 1.6–1.8; H: 1.5–2; white or tinged with red or yellow; taste: like common alum; result of volcanic action and decomposition of pyrite; Occ.: Tyrol, Bohemia, Vesuvius, Hungary, Peru, Bolivia, Argentina, New South Wales, Canary Islands, Smoky Mountain (N. C.), Gila River (N. M.).

Aluminum Hydroxide.—See **Gibbsite** and **Hydrargillite.**

Alum.—See **Kalinite, Mendozite,** and **Tschermigite.**

Amethyst.—See **Quartz.**

Amber.—(Succinite); sp. gr.: 1.050–1.096; H: 2—nearly 3; yellowish, orange, reddish brown, violet, blue, green, white, glassy; amorphous; Occ.: Baltic region of E. Prussia and elsewhere in Germany, Netherlands, Denmark, Sweden, Norfolk coast of England. Widely distributed in the Tertiary of Russia. Other gums and resins resembling amber occur with it also in Sicily, Rumania, Bohemia, Galicia, Austrian region, Apennines, Spain, Syria, Japan, Greenland, Mexico, South America, Maryland, Virginia and elsewhere.

Ammonium Chloride.—See **Salmiak.**

Anhydrite.—$CaSO_4$; rhombic, holohedral; sp. gr.: 2.9–3.0; H: 3–3.5; colorless to white, violet to blue, reddish gray, etc.; changes slowly to gypsum by hydration; Occ.: widespread.

Anhydritite.—(Halo-anhydrite); eutectic mixture of halite and anhydrite. Not infrequent in rock-salt deposits.

Apatite.—$Ca_5(PO_4)_3.F$ or $(Ca_5(PO_4)_3.Cl$; hexagonal; sp. gr.: 3.17–3.23; H: 4.5–5; sea green, bluish green, violet, blue, white, colorless, yellow, red, brown, etc. Soluble in HCl and HNO_3; in igneous and metamorphic rocks, veins, etc.; massive forms are phosphorites, etc.; Occ.: widespread.

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[1] A few metallic salts are included.

Aphthalose.—Same as *Aphthitalite.* Occ.: Kalusz.

Aphthitalite.—See **Glaserite.**

Aragonite.—$CaCO_3$; orthorhombic; sp. gr.: 2.93–2.95; H: 3.5–4; soluble like calcite; as oölites and pisolites and as organic calcite; Occ.: widespread.

Ascharite.—$3Mg_2B_2O_5.2H_2O$; sp. gr.: 2.45; H: 3–4; white, probably an alteration product from boracite; Occ.: Stassfurt salt deposits.

Asphaltum.—(Solid Bitumen); sp. gr.: 1.1–1.2; H: 1–2; black, honey yellow in thin sections; includes many varieties—albertite, grahamite, impsonite, uintaite, gilsonite, wurtzilite, chapapote, etc.; Occ.: throughout the world.

Astrakanite.—$Na_2SO_4.MgSO_4.4H_2O$ (may take up 1 per cent. K_2SO_4); monoclinic; sp. gr.: 2.22–2.28; H: 2.5–3.5; colorless, gray, bluish, green, red, orange; readily soluble in H_2O; Occ.: Kalusz, salt lakes of Astrachan, Argentina, near Mendoza and San Juan, North Chile, India (Mayo salt mine), Soda Lake (Cal.). Estancia Valley (N. M.).

Baeumlerite.—$CaCl_2.KCl$; sp. gr.: 2.2; white, sometimes stained violet, transparent to translucent; taste: bitter; deliquesces readily; Occ.: Hanover.

Bakerite.—$8CaO.5B_2O_3.6SiO_2.6H_2O$; sp. gr.: 2.73–2.93; H: 4.5 white to greenish; Occ.: in borax deposits.

Barite.—$BaSO_4$; orthorhombic; sp. gr.: 4.3–4.6; H: 2.5–3.5; colorless, white or variously tinted; in veins, beds, etc., in limestone and other rocks; Occ.: widespread.

Barrandite.—$(AlFe)PO_4 + 2H_2O$ or $(Al, Fe)_2O_3.P_2O_5.4H_2O$; sp. gr.: 2.576; H: 4.5; translucent to opaque; lustre: vitreous to greasy; pale bluish, reddish, greenish or yellowish gray; streak: yellowish to bluish white; Occ.: Cerhovic (Bohemia).

Bauxite.—Impure **Hydrargillite.**

Bechilite.—(Borocalcite) $CaB_4O_7.4H_2O$ or $CaO.B_2O_3.4H_2O$; Occ.: Tuscan borax lagoon, Salina Grandes (Argentina).

Bengal Saltpeter.—See **Saltpeter.**

Bischofite.—$MgCl_2.6H_2O$; monoclinic; sp. gr.: 1.59; H: 1.5–2; white, green, clear; 100 parts H_2O dissolves 255 grams at 0° and 920 grams at 100°; Occ.: Stassfurt salt beds.

Bitter Salt.—See **Reichardtite.**

Bloedite.—See **Astrakanite.**

Bobierrite.—$Mg_3P_2O_8.8H_2O$; monoclinic; colorless to white; Occ.: guano beds of Mexillones (Chile).

Boracite.—(Stassfurtite); $Mg_7B_{16}O_{30}Cl_2$ or $MgCl_2.2Mg_3B_8O_{15}$; rhombic and isometric; sp. gr.: 2.57–3; H: 7; white, yellowish, greenish, rarely red; insoluble in H_2O, slowly but completely in HCl; Occ.: Stassfurt region and elsewhere in Germany and France.

Borax.—(Tinkal); $Na_2B_4O_7.10H_2O$; monoclinic; sp. gr.; 1.7–1.8; H: 2–2.5 colorless, yellow, green, gray; 100 parts H_2O dissolves 7.9 grams at 20°C., 119.7 grams at 90°C.; Occ.: Tibet, borax lagoons of Italy, Clear Lake (Cal.) Nevada, Searles Lake (Cal.).

Borocalcite.—See **Bechilite.**

Boronatrocalcite.—See **Ulexite.**

Boussingaultite.—$(NH_4)_2SO_4.MgSO_4.6H_2O$; monoclinic; sp. gr.: 1.68–1.72; white; soft; in water of boric acid lagoons; Occ.: Tuscany, especially at fumaroles of Monte Cerbole.

Brongniartite.—See **Glauberite.**

Brucite.—$Mg(OH)_2$; trigonal; sp. gr.: 2.388; H: 2.5; white to grayish, bluish or greenish; in phyllites, schists, limestones and serpentines.

Brushite.—$HCaPO_4.2H_2O$; monoclinic; sp. gr.: 2.208; H:2–2.5; lustre: pearly to vitreous and in part splendent, earthy when massive, or resinous; colorless to pale yellowish; transparent or translucent; in rock guano; Occ.: Aves Island and Sombrero.

Calcite.—$CaCO_3$; trigonal; sp. gr.: 2.713–2.723; H: 3; colorless, white and varied; slowly soluble in H_2O, easily with effervescence in HCl; Occ.: widespread.

Calcareous sinter. See **Calcite.**

Caliche.—See **Soda Niter.**

Carnallite.—$KCl.MgCl_2.6H_2O$; rhombic; sp. gr.: 1.6; H: 1; colorless to snow white, through impurities light red to brown, violet, greenish, bluish, seldom wine yellow or milky white, opalescent; hygroscopic; 100 parts H_2O dissolves 64.5 parts at 18.75°C. and at 25°C. about 85 per cent. of the KCl separates out; important source of potash; Occ.: Stassfurt deposits, Kalusz in Galicia, Maman in Persia.

Carnallitite.—(Halo-carnallite); eutectic mixture of halite and carnallite; more common than carnallite; Occ.: Stassfurt region, etc.

Carniole.—Semi-transparent chalcedony; Occ.: South America, East Indies, Arabia, Siberia, Japan, Queensland, etc.

Celestite.—$SrSO_4$; rhombic; sp. gr.: 3.9–4; H: 3–3.5; colorless, bluish, yellowish; soluble with difficulty in H_2O, more easily in HCl; Occ.: in limestones in U. S.; widespread; also in Stassfurt salts and Searles Lake (Cal.).

Chalcedony.—SiO_2; sp. gr.: 2.59–2.64; H: 7; secondary; massive in veins cryptocrystalline quartz; Occ.: widespread.

Chert.—See **Quartz.**

Chile Saltpeter.—See **Soda Niter.**

Chlorocalcite.—$CaCl_2$; readily soluble in H_2O; white incrustations and crystals as emanations; Occ.: Vesuvius. (= Hydrophyllite.)

Chlorothionite.—$K_2SO_4.CuCl_2$; bright blue crusts; emanations. Occ.: Vesuvius.

Chrysoberyl.—$BeO.Al_2O_3 + Fe$; rhombic; sp. gr.: 3.65–3.8; H: 8.5; light colored yellow; yellowish green and greenish yellow to yellow-brown, transparent; as gems, green (Alexandrite), yellow to blue color play (Cats eye or Cymophane).

Chrysoprase.—Green transparent chalcedony generally in veins in serpentine.

Ciplyte.—$4CaO.2P_2O_5.SiO_2$ (?); slightly soluble in H_2SO_4; in chalk, associated with phosphorite; Occ.: Ciply and other points in Belgium.

Colemanite.—$Ca_2B_6O_{11}.5H_2O$; sp. gr.: 2.39–2.42; H: 3.5–4; colorless to transparent; lustre: glassy to diamond; Occ.: Panderma (sea of Marmora), Salina Grandes (Argentina), Searles Lake (Cal.).

Collophanite.—$Ca_3P_2O_8$ H_2O or $3CaO.P_2O_5.H_2O$; sp. gr.: 2.7; H: 2–2.5: white to yellowish white; lustre: dull earthy; Occ.: guano beds.

Corundum.—Al_2O_3; Trigonal; sp. gr.: 3.95–4.10; H: 9; colorless, blue (sapphire), red (ruby), brown, green; in igneous rocks, schists and limestones; mixed with magnetite = emery, in vein-like pockets in amphibolite and limestone (Mass.); Occ.: Mass., N. Y., Turkey, India, Burma, Greece, etc.

Cryolite.—Na_3AlF_6; Monoclinic; sp. gr.: 2.95–3; H: 2.5; snow white to colorless, reddish, brownish to brick-red or black; lustre: vitreous to greasy or pearly; forms large body in granite and in Ivigtut (West Greenland), the outer part passes into granite; Occ.: Greenland, Urals, Pikes Peak.

Cyanochroite.—$K_2SO_4.CuSO_4 + 6H_2O$; bright blue crusts on lava; emanations; Occ.: Vesuvius.

Dahllite.—$2Ca_3P_2O_8.CaCO_3.\frac{1}{2}H_2O$; sp. gr.: 3.053; H: 5; pale yellowish white; lustre: resinous; as crust on bright red apatite; Occ.: Norway.

Darapskite.—$NaNO_3.Na_2SO_4.H_2O$; tetragonal, square tabular crystals; colorless, transparent; with bloedite and soda niter; Occ.: Pampas del Toro, Atacama Desert.

Diamond.—C; Isometric; sp. gr.: 3.516–3.525; H: 10; colorless to white, pale yellow, orange, red, green, blue and brown to black; in altered, igneous rock and in granites; Occ.: S. Africa, Arkansas, N. S. Wales; India.

Diaspore.—$AlO(OH)$; orthorhombic; sp. gr.: 3.3–3.5; H: 6.5–7; whitish, grayish, greenish gray, brown, yellow, colorless; with corundum in dolomites and schists, in igneous rocks; Occ.: France, U. S., etc.

Diatomaceous earth, see **Tripolite.**

Dietzeite.—$7CaI_2O_6.8CaCrO_4$; monoclinic; sp. gr.: 3.698; H: 3–4; dark gold yellow; lustre: vitreous; conchoidal fracture; Occ.: Atacama (Chile).

Dolomite.—$CaMgCO_3$; trigonal; sp. gr.: 2.8–2.9; H: 3.5–4; colorless, white, reddish and varied; soluble in hot HCl; Occ.: widespread.

Douglasite.—$2KCl.FeCl_2.2H_2O$; Occ.: Stassfurt deposits.

Dysodile.—Hydrocarbon; sp. gr.: 1.14–1.25; yellow to greenish gray; streak: shining; in thin leaves or folia, flexible and slightly elastic; ill-smelling on burning and very inflammable leaving infusorial shells as residue; Occ.: Melili (Sicily).

Emery.—Mixture of **corundum** (which see) and magnetite or hematite.

Epsomite.—(Reichardtite, Pikrite, Bittersalt, etc.) $MgSO_4.7H_2O$; rhombic; sp. gr.: 1.68; H: 2–2.5; white, gray; transparent to translucent; 100 parts H_2O dissolves 133 grams at 25°C.; efflorescence; Occ.: Stassfurt region (Germany), Hallstadt (Austria), Herrengrund (Hungary), Kalusz (Silesia), Volterra (Tuscany), Vesuvius (eruption of 1850–1855), as solution in mineral water at Epsom (England), Seidlitz, Pullna and Saidschütz (Bohemia); India, Montmartre (Paris), Spain, Chile; South Africa, etc.

Exanthalite.—See **Mirabilite.**

Flint.—See **Quartz.**

Fluor Apatite.—See **Apatite.**

Fluorite.—CaF_2; isometric; sp. gr.: 3.180–3.189; H: 4; white, yellow, green, red, violet-blue, sky blue, brown to bluish black; around fumaroles, veins in crystalline rocks, cavities in limestones, etc.: Occ.: widespread.

Gagates (Gagatite).—See **Jet.**

Gaylussite.—$CaCO_3.Na_2CO_3.5H_2O$; monoclinic; sp. gr.: 1.9–1.95; H: 2–3; white, yellowish white, transparent; slightly soluble in H_2O; in mud; Occ.: Searles Lake (Cal.), Ragtown (Nev.); Lagunilla (Venezuela).

Gerhardtite.—$Cu_4(OH)_6(NO_3)_2$; orthorhombic; sp. gr.: 3.426; H: 2; deep emerald green; transparent; lustre: vitreous; cleavage: perfect parallel to *c* axis yielding thin flexible laminæ; insoluble in H_2O; soluble in dilute acids; Occ.: copper mines in Ariz.

Geyserite.—See **Opal.**

Gibbsite.—See **Hydrargillite.**

Glaserite.—(Apthitalite) $KNaSO_4$ or $K_3Na(SO_4)_2$; content of K_2SO_4 ranges from 78.6 per cent. to 61.8 per cent.; ditrigonal, scalenohedral; sp. gr.: 2.695; H: 3–3.5; colorless, reddish, yellowish, gray; 100 parts H_2O dissolves 8.5 grams at 0°C. and 26.2 grams at 100°C.; rare; Occ.: Stassfurt deposits, lavas of Vesuvius, Racalmuta (Sicily), Kalusz.

Glauberite.—(Brongniartite) $Na_2SO_4.CaSO_4$; monoclinic; sp. gr.: 2.7–2.8; H: 2.5–3; colorless, white, gray, yellow, red; partly soluble in H_2O, separates into Na_2SO_4 and gypsum. In little water solidified to stony mass; also emanations of volcanoes; Occ.: salt beds of Germany, Spain, France, Austria, Sicily, India; Peru, Borax and Searles Lakes (Cal.) Death Valley (Cal.).

Glauber Salts.—See **Mirabilite.**

Graphite.—C; trigonal or amorphous; sp. gr.: 2.09–2.3; H: 0.5–2; iron black to dark steel gray; metamorphic mineral, more rarely in igneous rocks.

Gypsum.—$CaSO_4.2H_2O$; monoclinic; sp. gr.: 2.32; H: 1.5–2; colorless, white, red, yellow, gray, brown, occasionally greenish and bluish; massive white = alabaster, crystallized transparent = selenite, fibrous = satin spar; 100 parts H_2O dissolves 0.26 parts at 21°C.; Occ.: widespread.

Halite.—(Rock Salt, Sea Salt) NaCl; isometric; cubic; sp. gr.: 2.162 H: 2; colorless, white, red, yellow, gray, rarely blue or green; 100 parts H_2O dissolves 35.6 grams at 0°C., 39.1 grams at 100°C.; also emanations from volcanoes; Occ.: universal.

Halo-anhydrite.—(Anhydritite); eutectic mixture of halite and anhydrite, frequent occurrence.

Halo-carnallite.—(Carnallitite); eutectic mixture of halite and carnallite, Occ.: Stassfurt, etc.

Halo-kainite.—(Kainitite); eutectic mixture of halite (30 per cent.) and kainite; Occ.: Stassfurt.

Halo-kieserite.—(Kieseritite); eutectic mixture of halite and kieserite; Occ.: Stassfurt.

Halo-langbeinite.—(Langbeinitite) eutectic mixture of halite and langbeinite; Occ.: Stassfurt.

Halo-sylvite.—(Sylvinite); eutectic mixture of halite and sylvite; Occ.: Stassfurt.

Halotrichite.—(Iron Alum) $FeSO_4.Al_2(SO_4)_3 + 24H_2O$; monoclinic or triclinic; yellowish white; silky fibrous; dull and pulverulent on exposure; taste: inky astringent; Occ.: Bavaria, Persia, Finland; Solfatara, Copiapo, Chile, N. Y., N. M., Mex., etc.

Hanksite.—$9Na_2SO_4.2Na_2CO_3.KCl$; hexagonal; sp. gr.: 2.55; H: 3–3.5; clear transparent and almost colorless to yellowish and cloudy; soluble in H_2O; common as crystals in mud; Occ.: Searles Lake (Cal.).

Hannayite.—$Mg_3P_2O_8.2H_2(NH_4)PO_4.8H_2O$; sp. gr.: 1.893; yellowish; in guano beds; Occ.: Ballarat (Victoria).

Hartsalt.—(Kieserohalosylvite); eutectic mixture of kieserite, halite and sylvite; Occ.: Stassfurt.

Hauptsalt.—(Kieserohalocarnallite) eutectic mixture of kieserite, halite and carnallite; principle source of potash in Stassfurt region; Occ.: Stassfurt.

Hausmannite.—Mn_3O_4; tetragonal; sp. gr.: 4.722–4.856; H: 5–5.5; brownish black; a manganese ore in porphyry; Occ.: Thuringia, Hartz, Sweden, Nordmark.

Hayesine.—$CaO_2.2B_2O_3.6H_2O$ or $CaB_4O_7.6H_2O$; Occ.: Salinas Grandas (Argentina).

Heintzite.—(Heintzeite, Kaliborite) $KMg_2B_{11}O_{19}.7H_2O$; monoclinic; sp. gr.: 2.13; H: 4.5; colorless, white, faint-yellow; rare; scarcely soluble in H_2O, easily in HCl; Occ.: Stassfurt.

Heliotrope.—Spotted jasper.

Hieratite—K_2SiF_6; isometric; grayish; spongy; as stalactitic concretions with scales of sassolite; emanations of volcanoes; Occ.: Lipari Islands.

Hovellite.—See **Sylvite.**

Hyalite.—A transparent to translucent colorless form of opal; less easily dissolved in caustic alkali than other forms.

Hydrargillite.—(Gibbsite) $Al(OH)_3$; monoclinic; sp. gr.: 2.287–2.420; H: 2.5–3.5; white, yellowish, grayish, etc.; in igenous and metamorphic rocks, also in bauxite.

Hydroboracite.—$CaMgB_6O_{11}.6H_2O$; sp. gr.: 2.168; H: 2; white, reddish; almost insoluble in H_2O, easily in warm HCl; Occ.: Caucasus, Stassfurt region.

Hydrophane.—A white or light colored translucent form of opal which adheres to the tongue and becomes more translucent or transparent in water.

Hydrophilite.—See **Chlorocalcite.**

Ice.—H_2O; hexagonal; sp. gr.: 0.9167; H: 1.5; colorless and transparent to white and translucent; Occ.: widespread.

Iceland Spar.—See **Calcite.**

Jasper.—Dense deeply colored (red, brown, yellow, green) semiopaque quartz; Occ.: widespread.

Jet.—(Gagates or Gagatite); hydrocarbon; sp. gr.: 1.35; H: 3–4; deep black; conchoidal fracture: dense and compact; mostly Jurassic and younger; Occ.: Whitby (England), Austria and Aragon (Spain), Southern France, south Germany, Bornholm, Russian Poland, French Indo-China, Colorado, Maryland.

Kainite.—$KCl.MgSO_4.3H_2O$; monoclinic; sp. gr.: 2.067–2.188; H: 2.5–3; white or colorless to dark flesh red; with halite and picromerite in thick beds or masses; Occ.: Stassfurt, Kalusz, Ascherleben.

Kalinite.—(Potash Alum) $KAl(SO_4)_2.12H_2O$; isometric; sp. gr.: 1.75; H: 2.5; white, vitreous, transparent or translucent; taste: astringent; soluble in water; rare in nature.

Kieserite.—$MgSO_4.H_2O$; monoclinic; sp. gr.: 2.569; H: 3–3.5; white, grayish white to yellowish; translucent to opaque; slowly soluble in H_2O, 100 parts H_2O dissolves 41.9 parts; with carnallite, halite and gypsum; Occ.: Stassfurt.

Kieseritite.—(Halo-kieserite); eutectic mixture of halite and kieserite; Occ.: Stassfurt.

Kieserohalocarnallite.—See **Hauptsalt.**

Kieserohalosylvite.—See **Hartsalt.**

Koenenite.—$2MgCl_2.3MgO.Al_2O_3.8H_2O$ or $6H_2O$; ditrigonal; scalenohedral; sp. gr.: 1.98; very soft, white, gray, brown; inclusions in rock salt; Occ.: Stassfurt, etc.

Kremersite.—$K(NH_4)FeCl_5.H_2O$; isometric; ruby red; easily soluble in H_2O; a metasalt; Occ.: emanations from Vesuvius.

Krugite.—$K_2SO_4.4CaSO_4.MgSO_4.2H_2O$; massive crystalline; sp. gr.: 2.801; H: 3.5; like polyhalite; Occ.: Stassfurt, Hallstadt, Ischl, etc.

Ktypeite.—$CaCO_3$; orthorhombic; sp. gr.: 2.58–2.70; H:. 3.5–4; pisolites; Occ.: Carlsbad (Bohemia) and Hamman-Meskutin (Algeria).

Lagonite.—$Fe_2O_3.3B_2O_3.3H_2O$; yellow; earthy; incrustations; Occ.: Tuscany.

Langbeinite.—$K_2SO_4.2MgSO_4$; tetrahedral; isometric; sp. gr.: 2.81; H: 3–4; transparent, colorless, yellow, red; slowly soluble in H_2O; a secondary mineral; Occ.: German potash beds, Mayo Mines (India).

Langbeinitite.—(Halolangbeinite); a eutectic mixture of halite and langbeinite; Occ.: Stassfurt.

Larderellite.—$(NH_4)_2B_8O_{13}.4H_2O$; monoclinic; sp. gr.: 1.477; white to yellowish; tasteless; small fibrous crystals; Occ.: Tuscany.

Lautarite.—$Ca(IO_3)_2$; monoclinic; sp. gr.: 4.59; colorless to yellowish; large prismatic crystals weighing as much as 20 grams; slightly soluble in H_2O; often embedded in bands of gypsum; Occ.: Atacama Desert (Chile).

Lazulite.—$2AlOH.MgPO_4.FePO_4$; monoclinic; sp. gr.: 3.057–3.122; H: 5–6; azure blue to bluish white; in veins and pockets; Occ.: United States, Sweden, Austria, etc.

Leonite.—$K_2SO_4.MgSO_4.4H_2O$; often with considerable Na_2SO_4; monoclinic; white, yellowish, greenish, pale violet; rare; easily soluble in H_2O; in concentrated solutions, K_2SO_4 separates out; Occ.: Stassfurt region.

Leopoldite.—See **Sylvite.**

Loeweite.—$2Na_2SO_4.2MgSO_4.5H_2O$; tetragonal; sp. gr.: 2.376; H: 2.5–3; yellowish white to flesh color; easily soluble in cold H_2O and changes to Astrakanite; rare; Occ.: Stassfurt region, Ischl salt mine (Austria).

Loewigite.—(Ignatievite) $K_2O.3Al_2O_3.4SO_3.9H_2O$; amorphous; sp. gr.: 2.58; light yellow; soluble in HCl; left on solution of carnallite; often in coal; Occ.: Zabıze (upper Galicia), La Tolfa (Italy), Muszai (Hungary), Bakhmut district (south Russia).

Lydite.—Black carbonaceous quartz rock.

Magnesite.—$MgCO_3$; trigonal; sp. gr.: 3.0–3.12; H: 3.5–4.5; white, yellowish, grayish white, brown; not soluble in cold HCl; in metamorphic schists and altered magnesian rocks; Occ.: Stassfurt salt clays, widespread.

Magnesium Hydroxide.—$Mg(OH)_2$ (see **Brucite**); residue of carnallite; Occ.: Stassfurt salt clays.

Makite.—See **Thenardite.** Double sulphate + carbonate soda; Occ.: Armenian Lakes.

Mamanite.—See **Polyhalite.**

Manganite.—$Mn_2O_3.H_2O$; orthorhombic; sp. gr.: 4.2–4.4; H: 4; steel gray to iron black, submetallic; Occ.: Harz, Thuringia, Scandinavia, British Isles, etc.

Martinite.—$2H_2Ca_5(PO_4)_4.H_2O$; rhombohedral; sp. gr.: 2.894; white to yellowish transparent; Occ.: Curaçao guano beds.

Martinsite.—See **Kieserite.**

Mendozite.—(Soda Alum) $NaAl(SO_4)_2.12H_2O$; isometric; other characters as in Kalinite.

Metabrushite.—$2HCaPO_4.3H_2O$; monoclinic; sp. gr.: 2.288–2.362; H: 2.5–3; pale yellow, buff to nearly white; from guano beds; Occ.: Sombrero (West Indies).

Minervite.—$H_2KAl_2(PO_4)_3.6H_2O$; with phosphate of lime as a white plastic mass mixed with clay; Occ.: Grotte de Minerva (France).

Mirabilite.—(Glauber Salt, Exanthalite) $Na_2SO_4.10H_2O$; monoclinic; sp. gr.: 1.462–1.5; H: 1.5–2; colorless; 12.2 grams soluble in 100 grams H_2O at 0°C., 184 grams at 30°C.; Occ.: Hallstadt, etc. (Austria), Bosnia, Karabugas, Ebro Valey, Bompensieri (Sicily), Caucasus, Great Salt Lake and Lakes of Russian and Hungarian plains, Searles Lake, etc., Soda Lake (Cal.), Mexico, Colombia, Chile, Argentina, etc.

Monetite.—$HCaPO_4$; triclinic; sp. gr.: 2.75; H: 3.5; pale yellowish white; lustre: vitreous; semi-transparent; in thick isolated masses; in seams in gypsum and in crusts in cavities, in guano; Moneta and Mona Islands (West Indies).

Muriazite.—See **Anhydrite.**

Natron.—$Na_2CO_3.10H_2O$; monoclinic; sp. gr.: 1.423–1.473; H: 1–1.5; effervescent, very soluble in H_2O; crystallizes only below 20°C.; in springs, lakes, etc.: Occ.: Searles Lake, etc., widespread, especially on Asiatic steppes.

Natroalunite.—$KNa(Al(OH)_2)_3(SO_4)_2$; essentially like alunite, which see.

Natroborocalcite.—See **Ulexite.**

Natronkalisimonyite.—See **Astrakanite**: Occ.: Kalusz.

Natron saltpeter.—See **Soda Saltpeter.**

Newberyite.—$HMgPO_4.3H_2O$; orthorhombic; sp. gr.: 2.10; H: 3–3.5; white, easily soluble in cold HCl and HNO_3; from guano beds; Occ.: Mexillones (Chile), Ballarat (Victoria).

Niter.—See **Saltpeter.**

Nitrobarite.—$Ba(NO_3)_2$; isometric; colorless crystals in part covered by a brownish black coating, resembling wad; Occ.: Chile.

Nitrocalcite.—$Ca(NO_3)_2$; efflorescent milky white or gray tufts and masses; taste: sharp and bitter; very deliquescent; from limestone caves; Occ.: Kentucky, Arizona, etc., Hungary, Spain, Venezuela, etc.

Nitroglauberite.—$6NaNO_3.2Na_2SO_4.3H_2O$; a white salt as efflorescences; taste: bitter; from limestone caverns; with nitrocalcite.

Nitromagnesite.—$Mg(NO_3)_2.nH_2O$; white; taste: bitter; from limestone caves with nitrocalcite.

Nontronite.—$H_4Fe_2Si_2O_9$ or $Fe_2O_3.3SiO_3.5H_2O$; (Chloropal) sp. gr.: 1.727–1.870; H: 2.5–4.5; pale straw yellow, canary yellow greenish; opaque to sub-translucent; unctuous feel; Occ.: Nontron (Dordogne, France).

Northrupite.—$Na_2CO_3.MgCO_3.NaCl$; isometric; sp. gr.: 2.38; H: 3.5–4; colorless; glassy; slightly soluble in cold H_2O; readily decomposed in hot H_2O with separation of $MgCO_3$; Occ.: Searles Lake (Cal.).

Opal.—$SiO_2 + nH_2O$; amorphous; sp. gr.: 1.9–2.3; H: 5.5–6.5; colorless to multicolored; varieties: Hyalite, 3 per cent. H_2O; geyserite, 9–13 per cent. H_2O; precious opal, 10 per cent. H_2O; tripolite, organic opal; as alteration product or in igneous rocks, replacement of fossil wood in volcanic tuffs, etc.: Occ.: Yellowstone Park (Geyserite), Iceland; widespread.

Ozokerite.—C_nH_{2n} (earth wax) (C–85.17, H–14.3); sp. gr.: 0.94–0.97; greenish to greenish brown in reflected light, yellowish brown to hyacinth red in transmitted light; soft, putty-like; aromatic; soluble in turpentine, naphtha, etc.; burns; associated with petroleum; Occ.: Miocenic of Boryslaw (Galicia), Russia, Italy, England, Colorado, New Mexico, Arizona, Utah, Wyoming, Texas, New Jersey, Canada, New Zealand, North Africa.

Pandermite.—$Ca_8B_{20}O_{38}.15H_2O$; similar to Colemanite; white, massive, like fine marble; in gypsum; Occ.: Panderma (Black Sea).

Paracite.—See **Boracite.**

Periclase.—MgO; isometric; sp. gr.: 3.674; H: nearly 6; colorless to grayish, yellow to brownish, yellow to dark green, transparent to translucent; in dolomitic limestone (Sweden), zone of contact metamorphism (Tyrol), lavas (Vesuvius); Occ.: Sweden, Predazzo (Tyrol), Monte Somma, etc.

Phosphorite.—See **Apatite.**

Petroleum.—C_nH_{2n+2}; sp. gr.: 0.6–0.9; thick oils to liquid; colorless, yellow to greenish black; Occ.: especially in Ordovicic, Siluric, Devonic, Carbonic, Permic, Mesozoic and Tertiary sediments.

Pickeringite.—$MgSO_4.Al_2(SO_4)_3 + 22H_2O$; H: 1; white, yellowish, pale rose red; becomes pulverulent and white on exposure; taste: bitter to astringent; Occ.: Chile, Argentina, Colorado, Nova Scotia.

Pickrite.—See **Epsomite.**

Pierssonite.—$Na_2CO_3.CaCO_3.2H_2O$; orthorhombic; sp. gr.: 2.35; H: 3–3.5; colorless, transparent or darkened; slightly soluble in H_2O; scattered crystals; Occ.: Searles Lake (Cal.).

Pikromerite.—See **Schoenite.**

Pinnoite.—$Mg(BO_2)_2.3H_2O$; tetragonal: sp. gr.: 2.27–2.37; H: 3–4; sulphur yellow to straw color, occasionally green, rarely reddish or gray; soluble in acid; Occ.: Stassfurt.

Plagiocitrite.—$KNa(Fe(OH)_2)_3(SO_4)_2$; monoclinic or triclinic; sp. gr.: 1.881; yellow translucent; taste: astringent; Occ.: Stassfurt region.

Polyhalite.—(Mamanite) $K_2SO_4.2CaSO_4.MgSO_4.2H_2O$; monoclinic (?) or rhombic (?) sp. gr.: 2.77–2.78; H: 3.5; gray, red, occasionally white, yellowish or bluish; slowly decomposed in H_2O with solution of $MgSO_4$ and K_2SO_4 and separation of gypsum, and in concentrated solutions, of syngenite; at Stassfurt it forms the polyhalite layer and annual rings as original deposit, also secondary; Occ.: Stassfurt; Ischl, Hallstadt, etc. (Austria), Stebnite (Galicia), Vic (Lorraine), Maman (Persia).

Priceite.—$3CaO.4B_2O_3.6H_2O$; sp. gr.: 2.26–2.48; H: 3; probably same as pandermite; white; massive; friable, chalky, enclosing colemanite; Occ.: Oregon; Salina Grandes (Argentina).

Pyropissite.—(Wax Coal); a hydrocarbon; sp. gr.: 4.93–5.22; earthy brown to grayish brown; encrusts massive limestone; Occ.: Weissenfels near Halle.

Quartz.—SiO_2; trigonal hexagonal or amorphous (opal group); sp. gr.: 2.660; H: 7; clear transparent, white translucent to multi-colored, insoluble; Occ.: universal.

Reichardtite.—See **Epsomite.**

Rinneite—$FeCl_2.3KCl.NaCl$; Stassfurt.

Ruby.—Red gem **Corundum,** which see.

Rutile.—TiO_2; ditetragonal; sp. gr.: 4.2–4.3; H: 6–6.5; red to black; insoluble; secondary in carnallite; in many igneous and metamorphic rocks and minerals (as inclusions), also in sedimentary rocks; Occ.: widespread.

Salmiak.—NH_4Cl; sp. gr.: 1.528; H: 1.5–2; glassy transparent and colorless when pure, white, yellowish, grayish; easily soluble in H_2O; taste: bitter; volcanic sublimate and in burning coal heaps in guano and in rock salt; Occ.: Vesuvius, Stromboli, Etna, Volcano, Pelé, Kilauea, etc., and in solfataras at Pozzuoli, St. Etienne (France), Newcastle (Scotland), etc., Chincha Islands.

Saltpeter.—(Niter, Bengal Saltpeter) KNO_3; orthorhombic; sp. gr.: 2.09–2.14; H: 2; white, subtransparent; taste: saline and cooling; as white granular crusts or masses or minute needle-like crystals; easily soluble in H_2O; abundant in soil of India, Mississippi Valley and elsewhere; Occ.: widespread.

San Sebastian Salt.—See **Thenardite.**

Sapphire.—Blue gem **Corundum,** which see.

Sardite.—Brown semitransparent chalcedony used for ornamental purposes.

Sassolite.—H_3BO_3 or $B(OH)_3$, orthoboric acid, triclinic; sp. gr.: 1.4–1.5; H: 1; colorless or yellowish plates; lustre: like mother of pearl; slowly soluble in cold H_2O, readily in boiling H_2O; Occ.: fumaroles of Tuscany, California, Nevada, Caucasus, etc., hot springs of Chile, mineral waters of Wiesbaden, Aachen, Vichy, mother liquor of salina of Bex (Switzerland).

Satinspar.—See **Gypsum.**

Schatzelite.—See **Sylvite.**

Schönite.—(Pikromerite) $K_2SO_4.MgSO_4.6H_2O$; monoclinic; sp. gr.: 2.03; H: 2.7; colorless, white, reddish, yellowish; 100 grams H_2O dissolves 10.9 grams at 20°C., 26.2 grams at 100°C., small quantity of H_2O decomposes it by dissolving $MgSO_4$, leaving nearly pure K_2SO_4; Occ.: Stassfurt region, lavas of Vesuvius, Kalusz (Galicia).

Searlesite.—$Na_2OB_2O_3.4SiO_2.2H_2O$; monoclinic(?); white; soft; in spherulites and fibrous; contains theoretically about 17.15 per cent. boric acid; Occ.: in mud of Searles Lake at 540 ft.

Selenite.—See **Gypsum.**

Selenium.—Native element; emanations of Lipari volcanoes.

Selensulphur.—Mixture of selenium and sulphur; orange red or reddish brown; emanations of Lipari volcanoes.

Siderite.—$FeCO_3$; trigonal; sp. gr.: 3.83–3.88; H: 3.5–4; ash gray, yellowish or greenish gray, brown, brownish red, rarely green; soluble in HCl; as stratified deposits; in many places impure in clay, in limestone, also in crystalline schists; Occ.: widespread.

Siliceous Sinter.—See **Opal.**

Simonyite.—See **Astrakanite.**

Smithsonite.—$ZnCO_3$; trigonal; sp. gr.:4.30–4.45; H: 5; white, often grayish, greenish or brownish, sometimes green, blue or brown; subtransparent to translucent; as incrustations in fissures and cavities, as stratified deposits; Occ.: widespread.

Soda.—Na_2CO_3; found only as hydrous forms in nature; see **Gaylussite, Natron, Thermonatrite.**

Soda Niter.—(Cubic Niter, Chile Saltpeter); $NaNO_3$; rhombohedral; sp. gr.: 2.1–2.2; H: 1.5–2; white, reddish brown, gray, lemon yellow; transparent; lustre: vitreous; taste: cooling; 70 parts dissolve in 100 parts H_2O at 0°C., 80 parts at 15°C., and 125 parts at 65°C.; Occ.: Chile and Peru, Spain(?), Sicily, India, Transcaspia, Egypt, California, Colorado River, Mohave Desert, etc.

Spinel.—$MgO.Al_2O_3$; isometric; sp. gr.: 3.5–4.1; H: 8; often as transparent variously colored gem; a contact metamorphic mineral; in limestone, granite, etc.; Occ.: lavas of Monte Somma; Ceylon, Siam, U. S., etc.

Stassfurtite.—See **Boracite.**

Stercorite.—$HNa(NH_4)PO_4.4H_2O$; monoclinic; sp. gr.: 1.615; H: 2; white, stained yellowish brown, transparent, easily soluble in hot and cold water; Occ.: in guano beds.

Strontianite.—$SrCO_3$; orthorhombic; sp. gr.: 3.680–3.714; H: 3.5–4; pale green, white, gray, yellow, yellowish brown; in veins, limestone, etc.; Occ.: Strontian (Argyllshire), Giants Causeway, Schoharie (N. Y.), etc.

Struvite.—$NH_4MgPO_4.6H_2O$; orthorhombic; sp. gr.: 1.65–1.7; H: 2; yellowish to brown, white; slightly soluble in H_2O; tasteless; from guano deposits; Occ.: Skipton Caves (Victoria), Hamburg, Africa, etc.

Succinite.—See **Amber.**

Sulpho-borite.—$2MgSO_4.4MgHBO_3.7H_2O$; rhombic; sp. gr.: 2.44; H: 4–4.5; colorless to reddish; in residue of salt solution of Westeregeln, etc.

Sulpho-halite.—$Na_2SO_4.NaCl$; isometric; sp. gr.: 2.5; H: 3.5; faint greenish yellow, transparent; slowly soluble in H_2O; rare; Occ.: Searles Lake (Cal.). Half of the Cl may be replaced by F.

Sulphur.—S; orthorhombic; sp. gr.: 2.05–2.09; H: 1.5–2.5; yellow, grayish; soluble in carbon disulphide; associated with anhydrite and other salt deposits; from volcanic and fumarole regions, etc.; Occ.: widespread.

Sylvinite.—(Halo-sylvite); eutectic mixture of sylvite and halite; KCl 20 to 60 per cent. or over; Occ.: Stassfurt, etc.

Sylvite.—(Leopoldite, Schätzelite, Hovelite, etc.) KCl: Isometric; clevage: cubic; sp. gr.: 1.989; H: 2; transparent, milky reddish and yellowish; in Hartsalt, dark gray, red or brown; primary and secondary; 100 parts H_2O dissolves 28.5 grams at 0°C.; 36.4 grams at 25°C., 56.5 grams at 100°C.; in Stassfurt region in beds as thick as 1 meter, usually as sylvinite; also as volcanic sublimates; Occ.: Stassfurt, Kalusz (Galicia), etc., Vesuvius.

Syngenite.—(Kaluszite) $K_2SO_4.CaSO_4.H_2O$; monoclinic; sp. gr.: 2.603; H: 2.5; transparent and colorless; 100 parts H_2O dissolves 0.25 grams; between sylvite layers; Occ.: Kalusz (Galicia), Stassfurt.

Tachhydrite.—$CaCl_2.2MgCl_2.12H_2O$; rhombohedral; sp. gr.: 1.671–1.867; H: 1.5; wax yellow to honey yellow; very hygroscopic; 100 parts H_2O dissolves 160 grams at 18.7°C. with heat development; associated with carnallite, kainite and anhydrite; Occ.: Stassfurt region.

Thenardite.—(San Sebastian Salt, Pyrotechnite, Makite) Na_2SO_4; rhombic; sp. gr.: 2.68; H: 2.5; transparent, colorless, reddish; 100 parts H_2O dissolves 4.5 grams at 60°C.; transformed to Glauber salt at 32.4°C.; Occ.: Lava of Vesuvius, Lake Baikal, Lakes of Caspian Plain, Spain, Atacama Desert (Chile), Arizona, Searles Lake (Cal.) and elsewhere in North America.

Thermonatrite.—$Na_2CO_3.H_2O$; sp. gr.: 1.5–1.6; H: 1.5; alteration product from Natron.

Tinkal.—See **Borax.**

Tinkalcite.—See **Ulexite.**

Tripolite.—(Diatomaceous Earth) $SiO_2 + nH_2O$; composed of siliceous (opal) frustules of diatoms; often impure; Occ.: widespread.

Trona.—(Urao) $Na_2CO_3.NaHCO_3.2H_2O$; monoclinic; sp. gr.: 2.11–2.14; H: 2.5–3; glassy or transparent, white or stained by impurities; very soluble in H_2O; Occ.: Searles Lake, Soda Lake (Nev.), Mono and Owens Lakes and elsewhere.

Tschermigite.—(Ammonia Alum) $(NH_4)Al(SO_4)_2.12H_2O$; with characters of kalinite, rare in nature.

Turquois.—$2Al_2O_3.P_2O_5.5H_2O$; amorphous, sp. gr.: 2.6–2.8; H: 6; light green to blue; botryoidal and kidney-shaped forms; in fissures, in Tertiary trachyte, etc.; Occ.: Persia and elsewhere in Central Asia, Sinai peninsula, New Mexico, Arizona, California, New Jersey, Colorado, Nevada, and more rarely in Alabama, Mexico and Victoria (Australia).

Tychite.—$2MgCO_3.2Na_2CO_3.Na_2SO_4$; isometric; sp. gr.: 2.45; H: 3.5–4; colorless transparent; almost insoluble in hot H_2O; very rare; Occ.: Searles Lake (Cal.).

Ulexite.—(Boronatrocalcite) $NaCaB_5O_9.8H_2O$ or $Na_2O.2CaO.5B_2O_3.16H_2O$; sp. gr.: 1.65; H: 1; white balls of fibrous satiny structure; slightly soluble in hot H_2O; easily in HCl; Occ.: Nevada, Nova Scotia, Peru, Argentina, Chile, South Africa, etc.

Urao.—See **Trona.**

Vanthoffite.—$3Na_2SO_4.MgSO_4$; sp. gr.: 2.7; H: 2–3; colorless to white; with loeweite and astrakanite; Occ.: Stassfurt region.

Variscite.—$Al_2O_3P_2O_5.4H_2O$; orthorhombic; H: 4–5; gem stone similar to turquois; Occ.: Utah and Nevada.

Vivianite.—$Fe_3P_2O_8 + 8H_2O$; monoclinic; sp. gr.: 2.58–2.68; H: 1.5–2; colorless when unaltered, blue to green deepening on exposure, transparent to opaque on exposure; sectile, flexible, in thin laminæ; in shells as blue iron earth, in limonite and peat swamps, associated with organic remains; Occ.: Kertch (Black Sea), Greenland, Syria, Cornwall, New York (with stilbite in gneiss of Harlem), New Jersey, Maryland, Kentucky, California, etc.

Wardite.—$2Al_2O_3P_2O_5.7H_2O$; sp. gr.: 2.77; H: 5; very similar to variscite and forming incrustations on it; gem stone; Occ.: Nevada, Utah.

Water.—H_2O; sp. gr.: 1; liquid.

Wax Coal.—See **Pyropissite.**

Witherite.—$BaCO_3$; rhombic; sp. gr.: 4.2–4.3; H: 3–3.5; colorless, gray or yellowish white, botryoidal and other forms common; vein mineral; Occ.: widespread.

CHAPTER III

THE SEA AS A SOURCE OF SALINE DEPOSITS

The sea may be regarded as the source of perhaps the largest number of natural salts, and indeed some geologists and chemists regard sea water as the original source of nearly all of the natural salt deposits of any magnitude. Our definition of sea salts limits the term to such saline deposits as are directly separated from sea water by concentration, by chemical reactions, by organic activities, or in some other way. Before considering the salts thus derived, we will briefly discuss the sea itself, its subdivisions and physical characters, its chemical composition and the conditions under which the salts of the sea water may be abstracted.

THE SEA AND ITS SUBSIDIARY BODIES

The sea is the entire body of connected salt water which covers the surface of the earth. Its superficial area is estimated at 361.1 million square kilometers, and its maximum depth (Nero deep) is 9,636 meters. The total volume of sea water on the earth is estimated to be 1,330 million cubic kilometers or 319,087,500 cubic miles (Krümmel, 1907), and its total weight at about 138×10^{16} metric tons.[1]

The Oceans.—The sea naturally falls into several more or less distinct bodies which are designated oceans, and of which there are four. These in the order of their size are: (1) the Pacific Ocean, (2) the Atlantic Ocean, (3) the Indian Ocean, and (4) the Arctic Ocean. These oceans are intercontinental water bodies, lying between continental masses of which we recognize three: (*a*) *the Old World mass*, comprising the geographical continents of Europe, Asia, Africa and Australia, with their dependent continental island masses; (*b*) *the New World mass*, comprising North and South America, with Greenland and the islands of the West Indian group; and (*c*) the little known *Antarctic continent*.

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[1] A metric ton contains 1,000 kilograms, equivalent to 2,204.6 pounds avoirdupois. K. Karsten, 1894, puts the total volume at 1,285,935,211 cubic kilometers or 307,496,000 cubic miles.

The relationships of the oceans and continental masses are as follows:

The Pacific and Atlantic Oceans lie between all three continent masses.

The Indian Ocean lies between the Old World mass and the Antarctic.

The Arctic Ocean lies between the Old and New World masses.

The continental masses and the oceanic basins have probably been permanent earth features throughout geological history, though they have varied greatly in size and in outline. Probably all of the known lands have been flooded by sea water at one time or another, some parts frequently so, but according to our best knowledge they have never been deep sea, nor have the ocean basins ever been replaced by continents, the repeated assertions of some authorities notwithstanding. The author of this book holds firmly to the belief that these great earth features are original, and determined by the constitution of the earth's lithosphere. He is further convinced from extended palæogeographic studies that no satisfactory proof has yet been offered for the former existence of transoceanic land masses, except those around the margins of the oceans, and he believes that all connecting bodies which, it has been asserted, bridged the oceans, are postulated on the basis of an insufficient consideration of the teachings of stratigraphy and geographic distribution of organisms. It is true that the smaller oceans, the Arctic and the Indian, were at different periods much contracted, but that they were ever entirely eliminated is not positively shown by any known facts. The Atlantic too, during Palæozoic time, was much smaller than it is today, large land masses occurring on the northeast and on the west, which have since entirely disappeared. Other land masses may have existed on the south, but of this we have too little knowledge at present. The Central Atlantic basin, however, has, so far as our present knowledge permits us to judge, always been a deep-water body.

The Subsidiary Bodies.—The water bodies which border on the oceans are the mediterraneans, the epeiric seas, and the funnel seas. All of these lie within the continental masses and so are termed Intra-Continental seas. The former two have basins independent of the general ocean basin, so that on elevation they would become distinct land-enclosed lakes. The third is merely a prolongation of the ocean basin into the land. The characteristics of each group may now be considered.

Mediterraneans.—These are like oceans in miniature and generally divide the continental masses into continents. Thus the original or Roman mediterranean separates Europe and Africa. The Red Sea mediterranean lies between Africa and Asia. The China Sea and a group of smaller mediterraneans lie between Asia and Australia, and the Caribbean and Mexican mediterraneans (Gulf of Mexico) lie between North and South America.[1]

In essentials, the mediterranean has not only a distinct basin, so that some portion of it lies below the lowest part of its rim, but it further agrees with the oceans in that its floor descends to depths into which sunlight never penetrates. In the mediterraneans, as well as in the oceans, three distinct zones are recognizable, namely the *littoral*, the *pelagic*, and the *abyssal*. The littoral zone is that portion which chiefly lies around the margin of the ocean or the mediterranean, and in which the depth is not sufficient to prevent the sunlight from reaching the bottom. In round numbers, the limit of this zone is at the 100 fathom line, or perhaps better, the 200 meter line, though local variations occur. In the oceans this littoral zone constitutes the water body which covers the continental shelf, in the mediterraneans it generally lies only above a narrow marginal shelf. Beyond this shelf the slope of the bottom descends to the greater depths, generally at a more rapid rate, and this portion to which the sunlight never penetrates constitutes the abyssal zone. An in-

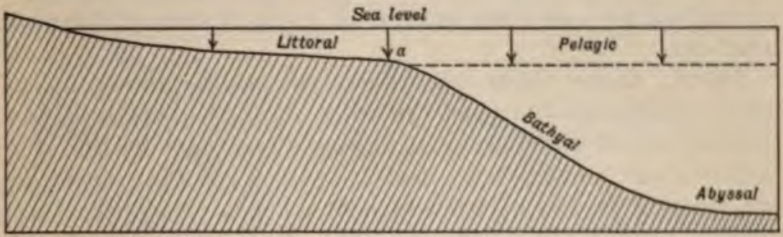

FIG. 1.—Diagrammatic cross-section of the sea shore, showing the principal zones. *a*, Edge of continental shelf. The arrows indicate the depth to which sunlight penetrates.

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[1] See further Grabau, A. W., "Principles of Stratigraphy," pp. 106–115.

termediate zone, the bathyal, is frequently recognized lying approximately between 200 and 900 meters.

The pelagic zone comprises the upper strata of sea-water illuminated by sunlight. It overlies the water of the abyssal zone and grades into it through an intermediary dusk stratum. The pelagic zone might be regarded as the continuation of the littoral zone beyond the edge of the continental shelf of the oceans or the marginal shelf of the mediterranean. It has, however, no rock bottom as the other two zones have, but rests upon a stratum of water. Landward it telescopes the littoral zone, the two becoming essentially confluent except so far as sediments and organic beings are concerned.[1] The preceding diagram represents a partial cross-section of an ocean or a mediterranean, and shows the relation of the several zones. The arrows indicate the depth to which sunlight penetrates (Fig. 1).

Mediterraneans have as a rule not been permanent depressions throughout geologic time, though the basins of some of them are very old.

Epeiric Seas.—These differ from the mediterraneans in the absence of the abyssal zone. In other words, they are so shallow that no part of their bottom, or at most a very small portion of it, sinks below the 200 meter depth. As a result their floors are everywhere reached by sunlight, and this has a very important bearing on the nature of the deposits. Typical examples of modern epeiric seas are: Hudson Bay, the North Sea, the Baltic Sea, and the Yellow Sea.

Most of the seas of the past, in which the various marine formations from the Palæozoic to the Tertiary were deposited, were epeiric seas. Such seas may readily become fresh water bodies, as has been the case with the Baltic in the recent past; or they may dry up altogether by evaporation after elevation and separation from the ocean. It is in seas of this type, or on the margins of mediterraneans, rarely on the ocean margin, that the sea salts are generally deposited.

Both mediterraneans and epeiric seas may be divided into *land-locked types*, in which only a comparatively narrow connection with the ocean exists; and into *marginal types*, where the connections with the oceans are numerous, a considerable portion of the outer rim being submerged and marked only by shoals and islands.

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[1] For a fuller discussion, see Principles of Stratigraphy, Chapters XXVI and XXVII.

As illustrations of the land-locked mediterraneans, we may cite the original or Roman mediterranean, the Red Sea, and less typically the Gulf of Mexico (Mexican mediterranean). Land-locked epeiric seas are illustrated by Hudson Bay, and better still by the Baltic Sea. Marginal mediterraneans are: Japan, Okhotsk, and Behring Seas; while marginal epeiric seas are illustrated by the North Sea and the Irish Sea.

The Funnel Seas.—These are so named because they form funnel-like prolongations of the ocean into the land. Not only do the sides of such an intra-continental water body contract regularly, but the bottom likewise rises landward at a more or less regular rate, there being no pronounced depressions within the margin. As a typical example, the Gulf of California may be cited, this representing the narrow type (Californian type) with the floor gradually descending from the head to an abyssal depth, so that all three zones, the littoral, pelagic, and abyssal, are represented. The Gulf of California has a closed head, *i.e.*, no headward connection with any other marine body, though a river, the Colorado, discharges into it. The Gulf of Aden, on the other hand, the mouth of which opens into the Indian Ocean, has an open head, there being a connection across a shallow ledge with the Red Sea mediterranean of which it forms the only natural outlet. The Bay of Fundy is also a funnel sea, the floor of which never descends to abyssal depths (Fundyan type). It thus corresponds to the epeiric seas, among the independent group. The Gulf of Suez may be considered a funnel sea of the Fundyan type, with artificially opened head.

A third type of funnel sea is characterized by rapid divergence of the sides, thus resulting in a broad form. Of this the Bay of Biscay is the most typical example (Biscayan type). The Gulf of Cadiz is a Biscayan funnel sea with open head the Straits of Gibraltar connecting it with the Roman mediterranean. Both these examples have floors which gradually descend to abyssal depths.

LAKES

Though not a part of the sea, they may be mentioned for comparison. All completely enclosed water bodies with no inlet from the oceans are classed as lakes, whether their water is fresh, brackish, salt, or alkaline. Thus, the Caspian Sea is a lake, though at one time it probably was a mediterranean sea, having been connected with the oceans. Its separation was brought about by the uprising of barriers and the partial evaporation of the water, until its level stands today 26 meters (85 feet) below the sea, while its greatest depth is 946 meters, bringing the deepest part of its floor down to 972 meters below sea level. The Dead Sea is a salt lake with a depression of its surface of 394 meters below the nearby Mediterranean (*i.e.*, below sea level). It has a maximum depth of water of 357 meters. Great Salt Lake of Utah probably never was a cut-off remnant of the sea but is a shrunken fresh water lake, which has become highly saline by concentration. This and other inland lakes will be more fully considered later.

PLAYAS, SEBCHAS, TAKYRS, MARSHES, SALT VLEYS, ETC.

"In the low, flat-bottomed depressions of undrained desert basins the rivers at times of flood will spread out into extensive shallow lakes of temporary existence. In the Great Basin region of western North America one such temporary lake reaches a length of about 100 miles by a breadth of 12 to 15 miles but with the water scarcely more than a few inches deep. Here the fine silt of the river is deposited, gradually subsiding as the shallow lake evaporates. After complete evaporation a smooth, hard-baked surface remains, marked by sun-cracks and the tracks of animals which visited the spot before complete hardening of the mud had occurred. Raindrop impressions likewise remain on such a surface In structure the material is finely stratified, as may be seen on the sides of the sun-crack rifts. This constitutes the *playa* of the American deserts (Mexico and the southern United States), the *takyr* or *schala* of Asia, or the *sebcha* of Africa. Russell has described a number of such temporary playa lakes from the western United States. He finds them a characteristic feature of the greater part of the valleys of Nevada, the largest being in the Black Rock Desert in the northwestern part of the state. It forms during the winter months and reaches an area of from 450 to 500 square miles, but is seldom over a few inches in depth. Often after storms it is a vast sheet of liquid mud, a characteristic of many playa lakes. In a few hours or a few days the water of the lake may all evaporate, leaving a hard, dry and absolutely barren surface, cracked in all directions as the surface contracts in drying. 'The lake beds then have a striking resemblance to tesselated pavements of cream-colored marble, and soon become so hard that they ring beneath the hoof-beats of a galloping horse, but retain scarcely a trace of his foot-prints.' Around the margin of the lake is a belt of plain with desert vegetation, the transition to which is formed by a marshy tract which in summer is marked by an abundant efflorescence of salts.

"Mechanical analysis has shown that the material of the playa may be 100 per cent. clay, and that laterally it will gradually pass, through the addition of sands, into the surrounding eolian deposits. In limestone regions where siliceous rocks are wanting the material of the playa will be largely lime-mud, and this may be the origin of some of the finely bedded, sun-cracked calcilutytes of the American Siluric, where the percentage of lime and magnesium carbonates is seventy or less.

"If the playa lake exists for some time it may become stocked with certain forms of organisms, especially types whose eggs or larvæ can be transported by wind or by birds. The small crustaceans Estheria, Daphnia, and Cypris are characteristic of desert lakes, the first having been found in ponds which are dry for eleven successive months. When, as is frequently the case, salts are present in the sediment, these effloresce on the surface, and from their hygroscopic character keep the surface of the playa sufficiently moist to prevent the removal by the wind of the accumulated material, and further to catch all dust particles carried across the surface by the winds. Thus the surface of the playa becomes dusted over with a fine coating of sand or dust, this process being repeated as the salts rise to the surface of the newly added layer. Where salt is present in great abundance a moist, slippery surface with incrustations of salt results, thus forming *salinas*. When wet, their surface is impassable, but when dry a crust of hard salt of dazzling whiteness characterizes the salina. As already noted, the thickness which such a salt deposit may reach is practically limited only by the depth of the basin and the supply of the salt.

"The deeply cleft surface of the dry playa is not infrequently buried by the wandering sands of the desert, while the rifts between the polygonal blocks are filled with wind-blown material, or the mud of the next succeeding inundation, and so preserved. This is made possible by the rapidity with which the playa surface becomes flooded, a case being on record where a lake 10 to 15 kilometers wide and of immeasurable length, though only from an inch and a half to a foot in depth, came into existence in twenty minutes. It must, however, be noted, that the dried surface of the playa is not infrequently softened on being wetted, and that from swelling and flowage of the mud the cracks may be closed again before they are filled. In this manner many mud-cracked surfaces are obliterated. From preliminary experiments, Barrell concludes that 'a mud-cracked loam or silty clay, even when the sand particles are imperceptible to the fingers, is an unfavorable material for the preservation of its detailed surface features . . . Upon being wet by rain the rapid swelling and disintegration of the surface stratum would turn the surface of such a deposit into a creamy mud . . . ' On the other hand, 'a pure clay, slowly subsiding from quiet waters, and wet sufficiently long to become compact upon drying, would retain its mud cracks upon rewetting, either by rain previous to flooding or by the flood waters themselves.' When the newly deposited layer is a thin one it will curl up like shavings on drying and these clay shavings will be blown into the sand dunes, where, upon subsequent softening, they will be compressed into clay lentils or pebbles, and so become a constituent part of an otherwise pure sandstone."[1]

The name "marsh" is commonly applied to salt playas in southwestern North America, and many of these form an important source of sodium chloride and other salts. A number of these are described in Chapter XII. In the Veldt of South Africa, many hollows become excavated by animals and other agencies, and in these salt water may collect, which on evaporation leaves deposits of salt. These are called salt vleys and they are described in Chapter IX. The name *Subbakha* or *Summakha* is used in Arabia for salt crusts left behind after the drying up of a salt playa.

SALINITY OF THE SEA

The amount of mineral matter of all kinds in solution in a given water body constitutes the salinity of that body. It is generally expressed in parts per thousand, rather than in percentages, and may in general be ascertained by the evaporation of a liter (1,000 cc.) of water, when the number of grams which the residue weighs constitutes the salinity.[1] It is spoken of as the permillage of the salt content and the symbol ‰ is employed to designate it.[2]

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[1] A. W. Grabau, "Principles of Stratigraphy," pp. 602–604.

The average salinity of sea water is 35 permille, *i.e.*, 35 grams of salts of various kinds occur in a liter of normal sea water. This is the average of the three largest oceans, the salinity of the Arctic being less, especially on the surface (25.5 ‰ for surface, 34.8 ‰ average of entire volume), on account of the abundant supply of fresh water from melting snow and ice. Mediterranean seas, especially when land-locked and lying within the warmer belts, generally have a higher salinity, as in the case of the Red Sea, which has a surface salinity of 38.8, and of the Mexican mediterranean in which the surface salinity is 35.95 ‰. On the other hand, when such water bodies are plentifully supplied with fresh water by streams, and the connection with the ocean or with other salt water bodies is narrow, a decrease in salinity is observed. Thus the Black Sea, a mediterranean, has a surface salinity of only 18.3 ‰ while the average salinity of the entire volume is only about 22 ‰. Epeiric seas illustrate this decrease of salinity through influx of fresh water even more strikingly. The Baltic Sea, which at its outlet into the North Sea has the normal salinity of that body (34.2 ‰), quickly decreases eastward until the water is fresh in the Finnish Gulf. The average surface salinity of the Baltic is only 7.8 ‰, while its volume salinity is 10 ‰.

Total Salt Content of the Sea.—The total amount of salts in the sea water of the earth has been estimated to be 48,400,000,000 million metric tons. In volume this would give 21.8 million cubic kilometers,[3] a quantity sufficient, if spread over a level sea bottom of 361 million square kilometers (the area of the sea surface as a whole), to make a layer more than 60 meters thick, and of this, a layer 47.5 meters thick would be common salt (NaCl). The other salts would make layers of the following thicknesses:

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[1] There is, of course, an element of error here, owing to the different weights of water of varying salinity. But for all practical purposes this is so slight that it may be disregarded. In terms of solution we may say that the salinity is measured by the number of grams of the solute in one liter of the solution, not one liter of the solvent.

[2] This must not be confused with parts per million, as has been done in some books. Permille is parts per thousand as per cent. is parts per hundred.

[3] Approximately 5,100,000 cubic miles. Clarke estimates it from other data as a little more than 4,800,000 cubic miles.

$MgCl_2$	5.8 meters
$MgSO_4$	3.9 meters
$CaSO_4$	2.3 meters
Remaining salts	0.6 meters

The total mass of salt would form a continent three times the size of Europe as it appears above sea level.

COMPOSITION OF THE SEA SALTS

The salts of normal sea water are few in number, those of sodium predominating. Common salt (NaCl) forms nearly 78 per cent. of the total volume of the salts, while magnesium chloride comes next, forming over 10 per cent. of the total volume of the salts.

The following table represents the mean of 77 analyses of ocean water from various localities, obtained by the Challenger expedition (Dittmar). The average salinity was 35.6 ‰.

TABLE IV.—ANALYSIS OF THE SALINE MATERIAL OF OCEAN WATER CALCULATED IN IONS

Ions	Per cent. of total solids	Grams per liter of sea water
Cl	55.292	19.68
Br	0.188	0.07
SO_4	7.692	2.74
CO_3	0.207	0.08
Na	30.593	10.89
K	1.106	0.40
Mg	3.725	1.33
Ca	1.197	0.43
	100.000	35.62

Calculated as salts, the following composition and amounts may be taken as representative. (Table V.)

Dissolved oxygen, nitrogen, and carbon dioxide also form important elements in the composition of the sea water, the CO_2 being estimated to equal 18 times the amount contained in the air. Many other elements are present in minute quantities, these having been figured with the $CaCO_3$ in the following table.

TABLE V.—ANALYSES OF SALINE MATTER OF OCEAN WATER, CALCULATED AS SALTS

Salt	Molecular weight	Specific gravity	Per cent. total solids	Permillage or grams per liter	Tons per cubic mile of sea water[1]
NaCl....	58.5	2.17	77.758	27.213	131,526,080
$MgCl_2$...	95.3	2.18	10.878	3.807	18,399,360
$MgSO_4$...	120.4	2.65	4.737	1.658	8,012,480
$CaSO_4$...	136.1	2.97	3.600	1.260	6,089,440
K_2SO_4....	174.1	....	2.465	0.863	4,169,760
$CaCO_3$*..	100.0	2.72	0.345	0.123	583,520
$MgBr_2$...	184.3	....	0.217	0.076	367,360
Total..	.....	....	100.000	35.000	169,148,000

[1] 2,000 pounds, avoirdupois each.

* Including all traces of other salts.

With the exception of the lime salts, the composition of marine waters over the entire earth is a remarkably constant one. Van't Hoff has figured it in terms of molecules with the following results: For every 100 molecules of NaCl, there are

2.2 molecules of KCl
7.8 molecules of $MgCl_2$
3.8 molecules $MgSO_4$

Only slight variations in the proportional amounts of the ions given for ocean water in Table IV are found in the analyses of the salts of intracontinental seas. Even such water as that of the Baltic, with its low salinity (7.8 ‰) shows only very minor deviations in the percentages of the various ions. This shows that the Baltic is only diluted sea water with no additions or abstractions of salt.[1]

RESULTS OBTAINED THROUGH THE EVAPORATION OF SEA WATER

Experiments of Usiglio.—In 1849 the Italian chemist Usiglio[2] published his results on the evaporation of sea water from the Mediterranean at Cette.

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[1] For Analyses, see Clarke, Data of Geochemistry.

[2] Analyse de l'eau de la Méditerranée sur le Cotes de France, par J. Usiglio, Annales des Chem. Phys., 3d ser. Vol. XXVII, pp. 92–107, 1849· and Études sur la Composition de l'eau de la Méditerranée et sur l'exploitation des sels qu'elle contient. Ibid., pp. 172–191, Paris, 1849.

This is one of the regions on the south coast of France where salt is produced for commercial purposes by the evaporation of sea water. Usiglio collected the water at night at two points, one 3,000 meters, and the other 5,000 meters from shore, and from a depth of about 1 meter below the surface. This water had a density at 21°C. (69.8°F.)[1] of 1,0258 corresponding to 3.5° on the Baumé hydrometer, and a salinity of 38.45 permille.

Five liters were selected for each evaporation experiment, weighing 5,129 grams or 1,026 grams per liter. The water was placed in large porcelain dishes and these were set in a hothouse which by artificial heat was kept at a constant temperature of 40°C. (104°F.). The air was kept dry by a large quantity of quicklime, which was frequently renewed while the air was changed at intervals. From time to time the liquid was removed from the hothouse and cooled to the ordinary temperature (21°C.). It was then decanted and the saline deposit left in the dish was transferred to a filter, pressed dry, and weighed. The volume and density of the remaining liquid were taken.[2]

The average results of several experiments were summarized by Usiglio as given in Table VII on p. 54 to which is added the specific gravity or density of the water.

Two determinations of density are given in the table, the first from Ochsenius, reduced to 12.5°C., the second from Clarke.[3] The results in the table have been reduced to grams per single liter.

Preliminary analyses showed that the sea water contained the following quantities of salts.[4]

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[1] The instrument used by Usiglio appears to have been graded at this temperature for he says that at 21°C. distilled water had a density of 1 corresponding to the zero degree on the scale. The Baumé hydrometer (or more commonly Baumé scale) in common use is graded at 60°F. (15.5°C.) for liquids heavier than water.

[2] Due care was of course taken to avoid losses in weighing, etc. See Usiglio, pp. 173–174.

[3] Neither of these densities correspond absolutely to those given by Usiglio who did not give a complete series. Those of Ochsenius in the first column are very close to Usiglio's determinations.

[4] See composition of average sea water, p. 51.

TABLE VI.—USIGLIO'S ANALYSIS OF SEA WATER FROM CETTE

Salt	100 grams of sea water contained, grams	Grams per liter
Fe_2O_3	0.0003	0.003
$CaCO_3$	0.0114	0.118
$CaSO_4$	0.1357	1.392
$MgSO_4$	0.2477	2.541
$MgCl_2$	0.3219	3.302
KCl	0.0505	0.518
NaBr	0.0556	0.570
NaCl	2.9424	30.182
Water	96.2345	987.175
Total	100.0000	1025.800
$CaSO_4.2H_2O$	0.1716	1.76
$MgSO_4.7H_2O$	0.5051	5.181

In the next table the results of Usiglio's experiments are summarized.

As will be seen from this table, no salt was deposited until nearly half of the water was evaporated, and the salinity increased to 72.14 permille when the iron oxide and calcium carbonate began to separate out. When the water was reduced to 19 per cent. of its original volume, and the salinity of the liquid had reached about 202 permille, hydrous calcium sulphate ($CaSO_4.2H_2O$) or gypsum began to separate out, and this continued with increasing density until all of it had separated out, when the volume was 3 per cent. of its original volume, or the 5 liters had been reduced to 150 cc.

No sodium chloride was separated out until the water had been evaporated to less than one-tenth its original volume (9.5 per cent.) when the salinity had increased to 388 permille. At that point over three grams were separated out more or less abruptly.

The composition of the water at the separation of NaCl and $MgSO_4$ is summarized by Van't Hoff in Table VIII, on the basis of Usiglio's work.

As noted in Table VIII, the composition of average sea water may be expressed in terms of 100 molecules of NaCl, as follows (Van't Hoff): 100 NaCl; 2.2 KCl; 7.8 $MgCl_2$; 3.8 $MgSO_4$. This is practically the number of molecules contained in 1,000

TABLE VII.—ORDER OF SEPARATION OF SALTS FROM SEA WATER (USIGLIO, WITH ADDITIONS[1])

Degrees on the Baumé scale at 21°C.	Density of water at 12.5°C.	Density or specific gravity after Clarke	Balance after evaporation and removal of salts, in liters	Separation at the successive densities in grams								
				Sesqui-oxide of iron	Calcium car-bonate	Hydrous calcium sulphate	Sodium chloride	Magnesium sulphate	Magnesium chloride	Sodium bromide	Potassium chloride	Total salts separated out
				Fe_2O_3	$CaCO_3$	$CaSO_4 2H_2O$	NaCl	$MgSO_4$	$MgCl_2$	NaBr	KCl	
1	2	3	4	5	6	7	8	9	10	11	12	13
3.5	1.0258	1.0258	1.000									
7.1	1.0506	1.0500	0.533	0.0030	0.0642	......	......	......	......	......	......	0.0672
11.5	1.0820	1.0836	0.316	......	Traces	......	......	......	......	......	......	Traces
14.0	1.1067	1.1037	0.245	......	Traces	......	......	......	......	......	......	Traces
16.75	1.1304	1.1264	0.190	......	0.0530	0.5600	......	......	......	......	......	0.6130
20.60	1.1653	1.1604	0.1445	......	......	0.5620	......	......	......	......	......	0.5620
22.00	1.1786	1.1732	0.131	......	......	0.1840	......	......	......	......	......	0.1840
25.00	1.2080	1.2015	0.112	......	......	0.1600	......	......	......	......	......	0.1600
26.25	1.2208	1.2138	0.095	......	......	0.0508	3.2614	0.0040	0.0078	......	......	3.3240
27.00	1.2285	1.2212	0.064	......	......	0.1476	9.6500	0.0130	0.0356	......	......	9.8462
28.50	1.2444	1.2363	0.039	......	......	0.0700	7.8960	0.0262	0.0434	0.0728	......	8.1084
30.20	1.2627	1.2570	0.0302	......	......	0.0144	2.6240	0.0174	0.0150	0.0358	......	2.7066
32.40	1.2874	1.2778	0.023	......	......	......	2.2720	0.0254	0.0240	0.0518	......	2.3732
35.00	1.3177	1.3069	0.0162	......	......	......	1.4040	0.5382	0.0274	0.0620	......	2.0316
Total of salts separated				0.0030	0.1172	1.7488	27.1074	0.6242	0.1532	0.2224	......	29.9762
Remainder in mother liquor (0.0162 l.)				......	......	......	2.5885	1.8545	3.1640	0.3300	0.5339	8.4700
Total salts in 1 liter of sea water				0.0030	0.1172	1.7488	29.6959	2.4787	3.3172	0.5524	0.5339	38.4471
Total salts according to direct analysis of sea water by Usiglio				0.0030	0.1170	1.7600	30.1830	2.5410	3.3020	0.5700	0.5180	38.9940
Differences				......	+0.0002	−0.0112	−0.4871	−0.0623	+0.0152	−0.0176	+0.0159	−0.5469

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[1] Columns 2, 3, and 13.

molecules of water (precisely 1,064 molecules H_2O) at the beginning of separation of sodium chloride.

TABLE VIII.—COMPOSITION OF SEA WATER AT SEPARATION OF NACL AND $MGSO_4$ (AFTER USIGLIO, SUMMARIZED BY VAN'T HOFF)

	Specific gravity	Salt content in 100 grams of solution			
		NaCl	KCl	$MgCl_2$	$MgSO_4$
Original sea water.......	1.0258	2.9424	0.0505	0.3219	0.2477
On NaCl separation.....	1.21	22.223	0.405	2.442	1.8714
On $MgSO_4$ separation....	1.32	12.105	2.497	14.796	8.676

Usiglio made an analysis of the liquid when the hydrometer stood at 25 degrees, showing a density of 1.21 and a reduction to 11.2 per cent. of its original volume, *i.e.*, when the 5 liters had been reduced by evaporation to 560 cc. This is reproduced in Tables IX and X, the latter recalculated to ionic form. The salinity at this stage was 333.289 permille. In Tables XI and XII, Usiglio's analyses at 30 and 35 degrees of the Baumé hydrometer are given, corresponding to densities of 1.264 and 1.32, respectively.

TABLE IX.—COMPOSITION OF THE SEA WATER REDUCED BY EVAPORATION TO 11.2 PER CENT. OF ITS ORIGINAL VOLUME, AND A DENSITY OF 1.21 (25 DEGREES ON BAUMÉ SCALE), MODIFIED FROM USIGLIO

Salt according to Usiglio's calculations	Grams in 100 gr. of water	Grams per 1 liter of water (calculated)	Grams in 100 gr. of water by analysis
$CaSO_4$........................	0.1712	2.072	0.165
$MgSO_4$........................	1.8714	22.644	1.874
$MgCl_2$........................	2.4420	29.548	2.436
KCl	0.4050	4.900	0.402
NaBr........................	0.4320	5.227	0.428
NaCl........................	22.2230	268.898	22.209
Total........................	27.5446	333.289	27.514

The first column is obtained by analysis of various quantities of the condensed water for each element or acid, and by calculation for 100 grams of the water. The last column is the result of direct analysis of 100 grams of the water calculated for the salts.

The actual quantities of each element or acid found was as follows, calculated to 100 grams of this water (density 1.21) and recalculated by the author to ionic form.

TABLE X.—COMPOSITION OF 100 GRAMS OF SEA WATER EVAPORATED TO 11.2 PER CENT. OF ITS ORIGINAL VOLUME WITH DENSITY OF 1.21: RECALCULATED TO NORMAL FORM FROM USIGLIO

Ca	0.0504
Mg	1.0154
Na	8.8320
K	0.2130
SO_4	1.6030
Cl	15.4820
Br	0.3360
	27.5318

The value of these tables lies in the fact that the state of condensation here taken is the critical one. Up to this point, only the oxide of iron, the calcium carbonate, and 1.4660 grams of $CaSO_4.2H_2O$ had separated out, *i.e.*, 83.8 per cent. of the total of that salt All the other salts were still in solution, but began to be separated out on further condensation.

In the next two tables analyses of the water at 30 and 35 degrees of the Baumé scale are given corresponding to densities of 1.264 and 1.32, respectively. Table XII is calculated to the ionic form.

TABLE XI.—ANALYSIS OF SEA WATER CONDENSED TO 30 AND 35 DEGREES OF THE BAUMÉ SCALE

Calculated salts	Density 1.264, 30 degrees Baumé scale		Density 1.32, 35 degrees Baumé scale	
	Grams in 100 gr. water at 30°Bé.	Grams per liter of the condensed water	Grams in 100 gr. water at 35°Bé.	Grams per liter of the condensed water
$MgSO_4$	6.231	78.76	8.676	114.48
$MgCl_2$	8.041	101.60	14.796	195.31
KCl	1.449	18.32	2.497	32.96
NaBr	1.161	14.72	1.545	20.39
NaCl	16.830	242.80	12.105	159.79
Total	33.712	426.20	39.619	522.93

TABLE XII.—ANALYSIS OF SEA WATER CONDENSED TO 30 AND 35 DEGREES OF THE BAUMÉ SCALE, CALCULATED IN IONS

Ions	At 30 degrees Baumé, density 1.264	At 35 degrees Baumé, density 1.32
Mg	3.3900	5.6620
Na	6.8700	5.1030
K	0.7610	1.3100
SO_4	4.9314	6.8690
Cl	16.8380	19.4470
Br	0.9010	1.2005
Total	33.6914	39.5915

When the water had been reduced to 1.62 per cent. of its original volume, *i.e.*, when the 5 liters had been reduced to 81 cc., a *mother liquor* remained, with a salinity of 522.9 permille (52.29 per cent.), and this contained the following salts still in solution (hydrometer 35 degrees, density 1.32):

TABLE XIII.—SALTS IN SOLUTION OF MOTHER LIQUOR

	In 81 cc. the residue of 5 liters	In 16.2 cc. the residue of 1 liter	Calculated grams per liter
NaCl	12.9425	2.5885	159.8
$MgSO_4$	9.2725	1.8545	114.5
$MgCl_2$	15.8200	3.1640	195.3
NaBr	1.6500	0.3300	20.4
KCl	2.6695	0.5339	32.96
Total	42.3545	8.4709	522.96

At this stage, with the hydrometer at 35 degrees, irregularities in deposition had begun to be noticed, the difference in temperature between night and day affecting the deposit. It sometimes happened that potassium salt was formed when the density was only between 34 and 35 degrees. At night, sulphate of magnesium was deposited, which was partially redissolved during the day.

The various salts of the mother liquor were affected in general in the following manner. On further condensation above 35 degrees Baumé:

(*a*) Magnesium sulphate was deposited principally on lowering of the temperature as the heptahydrate, sometimes also by continued evaporation, when it contained only six molecules of water (hexahydrate).[1]

(*b*) Sodium chloride was deposited especially during the day at the moment of concentration of the liquid.

(*c*) The double sulphate of potassium and magnesium (the mineral Schönite, $MgSO_4.K_2SO_4.6H_2O$) is less soluble than the magnesium sulphate, and more soluble than potassium sulphate, and also more soluble in warm than in cold solution.[2] It is in general deposited on cooling, and an excess of sulphate of magnesium in the solution favors its deposition.

(*d*) The double chloride of potassium and magnesium (the mineral Carnallite, $KMgCl_3.6H_2O$ or $KCl.MgCl_2.6H_2O$ – K, 14.50; Mg, 9.05; Cl, 37.60; H_2O, 38.85) is deliquescent and very easily decomposed. It crystallizes well from the solution, but is unstable.

(*e*) The chloride of magnesium (the mineral Bischofite, $MgCl_2.6H_2O$) another deliquescent salt, becomes more dominant among the salts separating out in the degree in which the water is concentrated

By frequent decantations of the liquid from the salts deposited at 35 degrees and above, the following succession of deposits was determined, in water which was exposed in a shallow layer to the air at night. During the first night the water at 35 degrees density deposited a considerable quantity of nearly pure sulphate of magnesium. The water decanted in the morning had only a density of 32 to 33 degrees, but its composition was very different from that obtained by direct condensation to 32 degrees. During the decantation a part of the magnesium sulphate was redissolved, but most of it remained behind.

By evaporation of the decanted water during the next day, it deposited a mixture of sodium chloride and magnesium sulphate. Sometimes, but rarely, this deposit contained traces of potash salts.

The water decanted that evening, on cooling during the second night, formed a new deposit of sulphate of magnesium, analogous to that formed during the first night.

The third decantation next morning had a density of 33 to 34 degrees. Concentrated during the day, it formed a complex deposit of sulphate of magnesium, the double sulphate of magnesium and potassium (Schönite), chloride of sodium, and bromide and chloride of magnesium.

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[1] See studies of Van't Hoff.

[2] Water at 100°C. dissolves about 0.57 of its weight, and at 15 degrees only 0.18 of its weight.

The evaporation of the third decantation proceeded rapidly the liquor reaching a density of 33.50° in two to three hours, so that it was necessary to decant it before evening. Three to four hours before nightfall, at the time when the temperature began to decrease, a new deposit, composed only of the double chloride of potassium and magnesium (Carnallite) began to form. It continued to separate out during the night, becoming often mixed with the double sulphate of potassium and magnesium (Schönite).

The next day the water was again decanted and evaporated anew. It passed successively through the densities of 36°, 36°50, and 37° without forming a sensible deposit, until two or three hours after noon. The density and viscosity of the liquid was so great that the heat of the sun raised its temperature to 50°C. (122°F.). After three o'clock in the afternoon the abatement of the temperature provoked an abundant deposit of the double chloride of potassium and magnesium (Carnallite), which was very pure. The deposit continued to form during the night, and was sometimes mixed with sulphate of magnesium, formed when the cooling was very sudden or very great. It was possible to recognize from the aspect of the deposit, *i.e.*, from the manner in which the two salts alternated, the alternations of the temperature during the night.

When the water had attained a density of 38° and by cooling was reduced to 36 or 37 degrees, it deposited a large quantity of the salts which it still contained, retaining only a small quantity of $NaCl$ and $MgSO_4$ but a considerable proportion of $MgCl_2$. Potash salts were no longer present in appreciable quantity.

The last of the liquid, preserved until the Autumn, was exposed to a temperature of 5° to 6°C., and deposited much chloride of magnesium well crystallized ($MgCl_2.6\,H_2O$—Bischofite).

The order of deposition from the mother liquor was thus as follows:

1. (night) Reichardtite (Epsomite) ($MgSO_4.7H_2O$).
2. (day) Hexahydrate ($MgSO_4.6H_2O$), Halite ($NaCl$), rarely potash salts (KCl, etc.).
3. (night) Reichardtite ($MgSO_4.7H_2O$)

4. (day) Hexahydrate ($MgSO_4.6H_2O$).
   Schönite ($MgSO_4.K_2SO_4.6H_2O$)
   Halite ($NaCl$)
   Bischofite ($MgCl_2.6H_2O$)
   Magnesium bromide ($MgBr_2$).
5. (afternoon) Carnallite ($MgCl_2.KCl.6H_2O$).
6. (night) Carnallite ($MgCl_2.KCl.6H_2O$).
   Schönite ($MgSO_4.K_2SO_4.6H_2O$).
7. (day) practically no deposit.
8. (afternoon) Carnallite ($MgCl_2.KCl.6H_2O$).
9. (night) Carnallite ($MgCl_2.KCl.6H_2O$).
   Reichardtite ($MgSO_4.7H_2O$).
10. (autumn temp. of 5° to 6°C.) Bischofite ($MgCl_2.6H_2O$).

This apparently normal order of deposition of mother liquor salts will be of some significance in comparison with the successive zones of such salts found in a natural deposit such as that of Stassfurt in Germany (see Chapter XXIV). Here the succession is from below upward (above the rock salt with its anhydrite layers).

1. Polyhalite zone, containing Bischofite ($MgCl_2.6H_2O$ small quantity).

   Polyhalite $2(CaSO_4)\ MgSO_4.K_2SO_4.2H_2O$.

2. Kieserite zone, containing Halite ($NaCl$)	65 per cent.
Kieserite $MgSO_4,\ H_2O$	17 per cent.
Carnallite $KCl.MgCl_2.6H_2O$	13 per cent.
Anhydrite $CaSO_4$	5 per cent.
3. Carnallite zone, containing Carnallite ($KClMgCl_2.6H_2O$).	55 per cent.
Halite ($NaCl$)	26 per cent.
Kieserite ($MgSO_4.H_2O$)	17 per cent.
Anhydrite ($CaSO_4$)	2 per cent.

Also minor quantities of Kainite ($MgSO_4.KCl.3H_2O$) Sylvite (KCl) and other minerals.

4. Kainite layers with Kainite ($MgSO_4.KCl.3H_2O$).
5. Sylvinite or Hart salz layer with mixed Sylvite (KCl) and rock salt ($NaCl$) some Kieserite ($MgSO_4.H_2O$).
6. Schönite layer with Schönite ($MgSO_4.K_2SO_4.6H_2O$).
7. Salt clay.

The succession of Carnallite and Schönite is thus the same as in Usiglio's experiments. The Kainite is a modified salt of the Carnallite type but with 3 molecules of water instead of 6. The early deposits of the heptahydrate and hexahydrate of magnesium sulphate are represented in the Stassfurt region by the Kieserite deposits, the monohydrate.

In addition to the deposition of the salts of the mother liquor listed above, the experiments of Usiglio elucidated the order of deposition of the following salts from ocean water: Iron oxide (Fe_2O_3), Calcium Carbonate ($CaCO_3$), Gypsum ($CaSO_4.2H_2O$), Rock salt ($NaCl$). Among the important salts the origin of which is not explained by these experiments, are Anhydrite ($CaSO_4$) and the mother liquor salts Polyhalite and Kieserite, Kainite and the many rarer salts found with them. These experiments lacked those essential elements which are operative in the formation of salt deposits in nature, namely (1) long periods of time, (2) extensive changes of temperature during deposition, (3) pressure and accompanying development of heat during long periods, such as natural deposits are subjected to after burial under later deposits, and which furnish the condition for reactions between the original salts and the production of meta-salts. The work of Van't Hoff, next to be discussed, attempted to take account of these factors.

INVESTIGATIONS OF VAN'T HOFF AND HIS ASSOCIATES

Professor J. H. Van't Hoff, formerly of Amsterdam University but after 1896 a member of the faculty of the University of Berlin, has in collaboration with Professor Meyerhoffer and a number of other physical chemists and his students, carried on a series of elaborate investigations of the conditions and results of deposition of oceanic salts. These investigations have appeared from time to time since 1887 in various journals, especially the Zeitschrift für physikalische Chemie, and the proceedings of the Royal Prussian and the Imperial Viennese Academies of Science, and comprise more than 50 separate articles. Instead of working with ocean water, as did Usiglio, Van't Hoff undertook the study of the salts formed from such waters and obtained abundantly from the Stassfurt deposits. By solution and recrystallization of these salts in various proportions, and by the study of the effects of varying temperature and pressure, he has been able to solve many of the problems on the origin and condition of formation of these saline deposits.

The phases of these studies especially significant to the student of salt deposition deal (1) with the conditions of deposition under concentration of the salts from complex solutions, and (2) with the reaction of salts upon one another, under varying physical conditions and the production of complex salts. The latter phase will be referred to again under the chapters on Metasalts; of the first a brief summary may be given here.[1]

Van't Hoff designates the processes which result in the deposition of salts through concentration of the solutions containing them, changes in the conditions of equilibrium, both physical and chemical in their nature.

In all such studies the composition, both qualitative and quantitative, of the solution is of prime significance, while to a certain degree of equal importance is the solubility of the salts contained in it. In general, deposition of salts is in inverse order of their solubility, but, as will be shown presently, this is strongly influenced by the composition of the solution as a whole. This may be stated in the following way: The solubility of a salt in pure water differs materially from its solubility in water containing other substances in solution, whether these are salts or gases.

The simplest condition in Van't Hoff's solution experiments was under the pressure of a single atmosphere and the temperature of the laboratory, *i.e.*, 25°C. In order to produce saturation, a sufficient quantity of each of the required salts was added, so that portions of each remained on the bottom of the vessel in which the solution was made. These "bottom salts" (Bodensalze) as they are called, insure continued saturation by remaining in contact with the liquid (see *ante*-chapter I). If, then, two salts, such as $NaCl$ and KCl are present in sufficient quantity so that after prolonged stirring part of each remains as a bottom salt, a solution saturated for the two salts is produced. In this the quantities of each will be notably less than would be the case in two saturated solutions each containing only one of the salts. Figured on the basis of the number of molecules of the salt taken into solution in 1,000 molecules of pure water, the following results are obtained:

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[1] For a condensed summary of these studies, not always readily understood, however, without reference to the original articles, see J. H. Van't Hoff, Zur Bildung der Ozeanischen Salzablagerungen. Erstes Heft Braunschweig, Friedrich Vierweg and Sohn, 1905, and Acht Vorträge über Physikalische Chemie; Gehalten auf Einladung der Universität Chicago, 20 bis 24 Juni, 1901, Lectures 7 and 8, Die Physikalische Chemie und die Geologie, same publisher, 1902, pp. 61–81. See also J. A. Turrentiné, Bull. 94, Bureau of Soils, U. S. Dept. of Agriculture, 1913, pp. 68–81.

The discussion of the Stassfürt salt deposits, for the elucidation of the origin of which these studies were made, is taken up in Chapter XXIV (Vol. II).

TABLE XIV.—SATURATION OF WATER WITH NACL AND KCL AT 25°

Pure water saturated at 25°C. by	Number of molecules dissolved in 1,000 molecules of H_2O	
	NaCl	KCl
NaCl	111	
KCl	...	88
NaCl + KCl	89	39

If, now, a given solution of these two salts contains more NaCl than is demanded by the ratio 89 : 58.5 (mol. wt.[1] of NaCl) = 39 : 79.5 (mol. wt. KCl), sodium chloride will, on condensation, separate out first until the proper ratio is produced, whereas if the excess is KCl, that salt will be the first to separate. When the conditions of the above ratio are reached, *i.e.*, when the salt in excess has been separated out until 89 molecules of NaCl and 39 molecules of KCl remain for each 1,000 molecules of water, the condition of equilibrium of saturation for that solution is

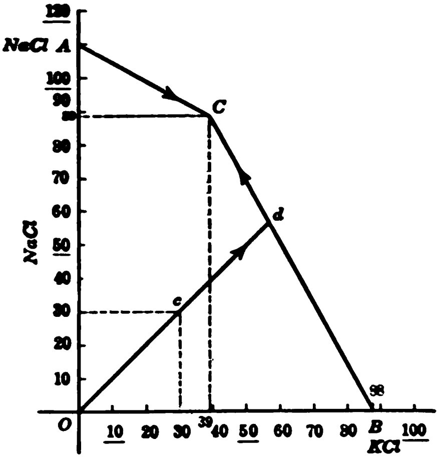

FIG. 2.—Saturation diagram for solutions of NaCl and KCl.

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[1] Better, formula weight.

reached, and thereafter, on further concentration, both salts will separate, while the composition of the liquid will remain constant. This relationship is expressed graphically in the preceding diagram (Fig. 2). In the two coördinates the solubility in pure water of NaCl (111) is indicated on the ordinate at *A*, and that of KCl (88) on the abscissa at *B*. The point *C* represents the solubility of each when both are present and is obtained by the intersection of lines from the ordinate at 89, the solubility of NaCl in the mixed solution, and the abscissa at 39, the solubility of KCl in the mixed solution. The line *A–C* will then represent saturation for NaCl with increasing content of KCl, while the line *B–C* represents saturation for KCl with increasing content of NaCl, *C* being the point of complete saturation for both.

Given, now, an unsaturated solution of these salts, in which the quantities of each (expressed in molecules) is indicated by the position of the point *c* within the polygon *O A C B*, say 30 molecules of each for every 1,000 molecules of water, on concentration by evaporation the composition of the solution will be the same, except that the quantities of each per 1,000 molecules of water will increase at a regular rate. This increase is expressed by the continuation of the line *Oc* to *d*, when the quantity of the two salts in the given case is approximately 57 molecules of each for every 1,000 molecules of water. From this point on, separation of KCl takes place on further condensation, the proportions thus changing, which is comparable to a movement along the line *d–C* toward *C*. When the condition expressed by *C* is reached, simultaneous separation of both salts takes place, which would continue until complete evaporation has resulted.

C, then, is the *crystallization point* for the KCl and NaCl solution. For other solutions the crystallization point *C* would, of course, have different positions.

If two salts combine to form a double salt, as, for example, $MgCl_2.6H_2O$ (Bischofite) and KCl (Sylvite) saturated at 108 and 88, respectively, to form Carnallite ($KClMgCl_2.6H_2O$), two saturation points are produced, one for KCl and Carnallite, which corresponds to the molecular ratio of $1{,}000H_2O$, 11KCl, 72.5 $MgCl_2$ (*E* in Fig. 3), and the other for magnesium chloride and Carnallite, which corresponds to the molecular ratio of $1{,}000H_2O$, 2KCl, $105MgCl_2$ (*F* in Fig. 3). This is shown graphically in the following diagram, where *E* and *F* represent the two saturation points, or points of crystallization respectively.

In Table XV, p 69, are given the crystallization points of salts from saturated solutions. The first group (*A D*) represents saturation for single salt only; in each solution, four salts, the chlorides and sulphates of potassium and magnesium being chosen. The number of molecules taken up by 1,000 molecules of water are given. For the sake of better comparison, equivalent quantities are used in the solutions, the potassium chloride being given as a double molecule, which reduces the number of molecules in the solution to half that found for the single molecule.

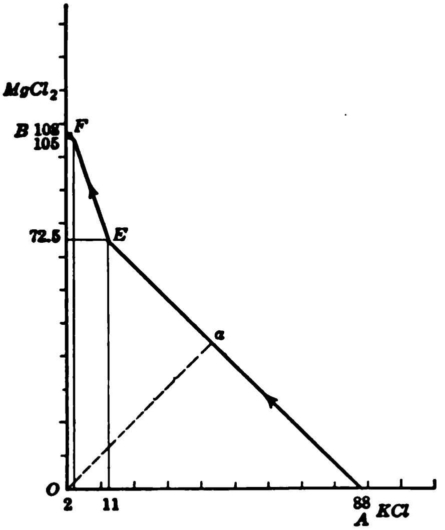

FIG. 3.—Saturation diagram for $MgCl_2$ and KCl at 25°C. The line *Oa* represents a solution saturated for carnallite alone ($KCl.MgCl_2.6H_2O$). The arrows indicate that at any point along the line *AE*, KCl will alone separate out until *E* is reached after which carnallite will also separate out until *F* is reached, when no more KCl separates but instead $MgCl_2.6H_2O$ and carnallite to complete evaporation.

The molecular ratio of these four salts is laid off on the coördinates in the following diagram (Fig. 4), at *A*, *B*, *C* and *D*.

The second series, *E* to *L*, represent saturated solutions of two salts, the same salts as above being chosen. Four mixtures of two salts each were made, two of these mixtures resulting in the formation of double salts, one forming a new hydrate, while only one of them (*A D*) remained a simple mixture. In the latter case, there is one crystallization point (Fig. 4*L*) for the two salts, but in the other cases, where a double salt or a new hydrate is formed, two crystallization points will arise, lying between those of the respective single salts.

The mixtures with their double salts or hydrates are:

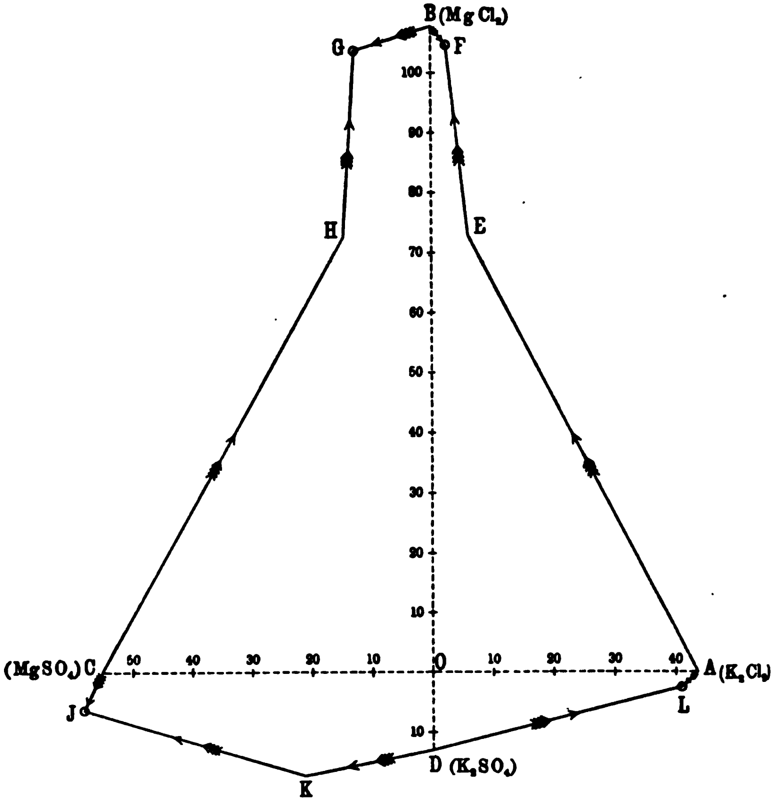

Fig. 4.—Saturation diagram for one and two salts at 25°C. and the double salts or hydrates produced. (*From Van't Hoff.*) (For significance of letters see Table XV, column 2. For location of saturation points see last four columns of Table XV.). Potassium chloride is here represented as the double molecule hence the line *OA* is only half as long, proportionally, as in Fig. 3. The arrows have the same significance as in Fig. 3.

Original salt	Double salt or hydrate
A. K_2Cl_2 B. $MgCl_2.6H_2O$	A + B = Carnallite ($KMgCl_3.6H_2O$).
B. $MgCl_2.6H_2O$ C. $MgSO_4.7H_2O$	B + C = Magnesium sulphohexahydrate ($MgSO._4.6H_2O$).
C. $MgSO_4.7H_2O$ D. K_2SO_4	C + D = Schönite ($MgSO_4.K_2SO_4.6H_2O$).
D. K_2SO_4 A. K_2Cl_2	D + A = No double salt or hydrate.

Potassium chloride occurs in nature as the mineral Sylvite. The mineral name Bischofite is given to the chloride of magnesium ($MgCl_2.6H_2O$) as it occurs in nature. The sulphate of magnesium with 7 molecules of water is the mineral Epsomite or Reichardtite, but the sulphate with 6 molecules of water has not so far been found in nature. In the present case it is produced from Epsomite by the dehydrating influence of magnesium chloride.

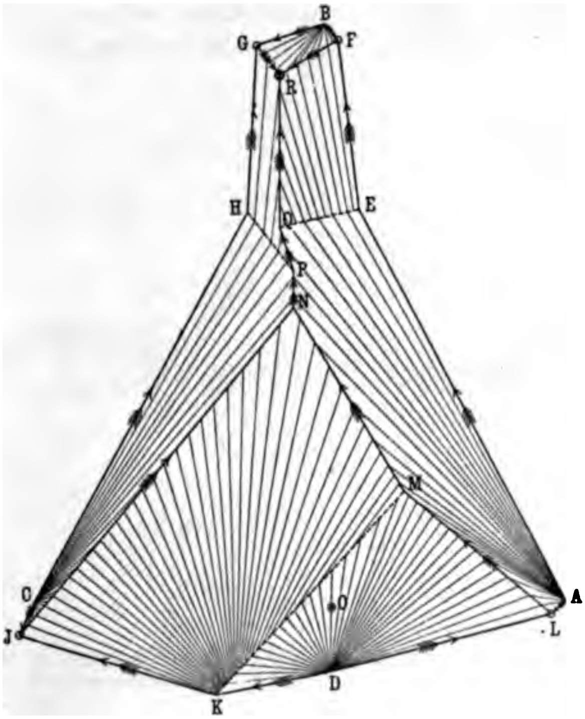

FIG. 5.—Saturation and crystallization diagram for three salts at 25°C. (*From Van't Hoff.*) (For significance of letters see Table XV, column 2.) The arrows have same significance as in preceding diagrams. The bundles of lines within the several fields have similar significance.

Two things must be kept in mind in the study of the diagram and table: (1) When two salts are introduced into the solution to the saturation of both, and a new salt is formed by their combination, there will be (*a*) two crystallization points, one for each of the original salts and the combination, and (*b*) there will be different amounts of each of the original two salts in the solution at each of the crystallization points. (2) Where the new hydrate is produced there will also be two crystallization points, one for each of the two original salts in the mixture, and the new hydrate. At each crystallization point there will then be different amounts of each of the two original salts in the solution.

When the original saturated solution contains three salts, two of which may combine to form a double salt or a new hydrate, the number of crystallization points becomes greater. The graphic representation requires a three-dimension diagram (Fig. 5), a figure composed of a number of polygonal fields, each of which corresponds to the saturation of a single salt as shown in the diagram (Fig. 6). The three salts, in terms of which the solution is expressed in the following table, are KCl, $MgCl_2$, and $MgSO_4$. It could have been expressed in the ions, or, instead of being calculated in terms of Potassium chloride and Magnesium sulphate, could have been given as Potassium sulphate and Magnesium chloride.

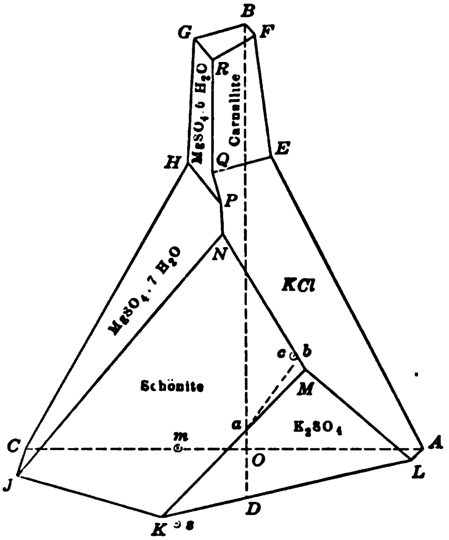

FIG. 6.—Saturation diagram for the various salts represented at 25°C. The lines and point of junction indicate paragenesis. (*Redrawn after Van't Hoff.*)

If to a large quantity of a solution saturated for KCL and K_2SO_4 magnesium is added, say in the form of sulphate, and the mixture slowly evaporated at 25°C., at first KCL and K_2SO_4 will

TABLE XV.—NUMBER OF MOLS. OF SALT IN 1,000 MOLS. OF WATER AT THE CRYSTALLIZATION POINTS WHEN THE WATER IS SATURATED WITH ONE, TWO, AND THREE SALTS

Water saturated with	Saturation or crystallization point for	Number of mols. of salt dissolved in 1,000 mols. of water at 25°C.			
		K_2Cl_2	$MgCl_2$	$MgSO_4$	K_2SO_4
I. One Salt					
A. KCl	*A.* KCl	44.0			
B. $MgCl_2.6H_2O$	*B.* $MgCl_2.6H_2O$	....	108.0		
C. $MgSO_4.7H_2O$	*C.* $MgSO_4.7H_2O$	....	......	55.0	
D. K_2SO_4	*D.* K_2SO_4	....	......	....	12.0
II. Two Salts					
A.B. KCl, $MgCl_2.6H_2O$	*E.* KCl and Carnallite	5.5	72.5		
A.B. KCl, $MgCl_2.6H_2O$	*F.* $MgCl_2.6H_2O$ and Carnallite	1.0	105.0		
B.C. $MgCl_2.6H_2O$, $MgSO_4.7H_2O$	*G.* $MgCl_2.6H_2O$ and $MgSO_4.6H_2O$	....	104.0	14.0	
B.C. $MgCl_2.6H_2O$, $MgSO_4.7H_2O$	*H.* $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$	....	73.0	15.0	
C.D. $MgSO_4.7H_2O$, K_2SO_4	*J* $MgSO_4.7H_2O$ and Schönite	....	......	58.5	5.5
C.D. $MgSO_4.7H_2O$,K_2SO_4	*K.* K_2SO_4 and Schönite	....	......	22.0	16.0
D.A. K_2SO_4, KCl	*L.* K_2SO_4 and KCl	42.0	......	....	1.5
III. Three Salts					
A.D.C. KCl, K_2SO_4, $MgSO_4.7H_2O$	*M.* KCl.K_2SO_4 and Schönite	25.0	21.0	11.0	
	N. KCl.$MgSO_4.7H_2O$ and Schönite	9.0	55.0	16.0	
	P. KCl.$MgSO_4.7H_2O$ and $MgSO_4.6H_2O$	8.0	62.0	15.0	
	Q. KCl, Carnallite and $MgSO_4.6H_2O$	4.5	70.0	13.5	
	R. $MgCl_2.6H_2O$ Carnallite and $MgSO_4.6H_2O$	2.0	99.0	12.0	

separate out. On removing these evaporates as they are formed day by day, the double salt Schönite ($MgSO_4.K_2SO_4.6H_2O$) will after a while begin to separate out. At this point the saturation or crystallization point for Schönite and the two potassium salts is reached, as expressed in *M* in the diagram (Fig. 6). The solution is then a constant one for the three salts. Four other constant solutions are possible, as indicated in the combinations given under *N*, *P*, *Q* and *R*.[1]

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[1] See for details R. Löwenburg Zeitschr. f. phys. Chemie 13, p. 459, 23, p. 98, with Meyerhoffer: Sitzungsber, d. Kgl. preuss. Akad. d. Wissenschaften, 1897, p. 1019; also Bash: Ueber Künstliche Darstellung von Polyhalite. Inauguraldissertation, Berlin, 1901, p. 18.

Solutions Saturated for Sodium Chloride and Other Salts

The preceding examples illustrate the general principles involved in the concentration of solutions containing one, two, or three salts. Ocean water, however, when sufficiently concentrated to reach the stage of saturation for mother-liquor salts, is always saturated for sodium chloride as well, the excess of which has already separated out during the earlier stages of concentration. Moreover, common salt is always deposited with the mother-liquor salts, occurring in association with all of them.

In the following tables from Van't Hoff, the character of solutions saturated for sodium chloride and one or more of the other salts is given at the crystallization points: *A*, for 25° and *B*, for 83°C.

TABLE XVI, *A*.—COMPOSITION OF SOLUTION SATURATED FOR SODIUM CHLORIDE AND OTHER SALTS IN EQUILIBRIUM AT 25°C.

	Saturated for NaCl and			1,000 mols. H_2O in mols.				
				Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Na_2SO_4
O	....	....	....	55.5				
A	$MgCl_2.6H_2O$	....	....	1.0	....	106.0		
B	KCl	....	....	44.5	19.5			
C	Na_2SO_4	....	....	51.0	....	....	.....	12.5
D	$MgCl_2.6H_2O$	Carnallite	....	1.0	0.5	105.0		
E	KCl	Carnallite	....	2.0	5.5	70.5		
F	KCl	Glaserite	....	44.0	20.0	....	.....	4.5
G	Na_2SO_4	Glaserite	....	44.0	10.5	....	.....	14.5
H	Na_2SO_4	Astrakanite	....	46.0	....	....	16.5	3.0
I	$MgSO_4.7H_2O$	Astrakanite	....	26.0	....	7.0	34.0	
J	$MgSO_4.7H_2O$	$MgSO_4.6H_2O$	....	4.0	....	67.5	12.0	
K	$MgSO_4.6H_2O$	Kieserite	....	2.5	....	79.0	9.5	
L	Kieserite	$MgCl_2.6H_2O$	....	1.0	....	101.0	5.0	
M	KCl	Glaserite	Schönite	23.0	14.0	21.5	14.0	
N	KCl	Schönite	Leonite	19.5	14.5	25.5	14.5	
P	KCl	Leonite	Kainite	9.5	9.5	47.0	14.5	
Q	KCl	Kainite	Carnallite	2.5	6.0	68.0	5.0	
R	Carnallite	Kainite	Kieserite	1.0	1.0	85.5	8.0	
S	Na_2SO_4	Glaserite	Astrakanite	42.0	8.0	....	16.0	6.0
T	Glaserite	Astrakanite	Schönite	27.5	10.5	16.5	18.5	
U	Leonite	Astrakanite	Schönite	22.0	10.5	23.0	19.0	
V	Leonite	Astrakanite	$MgSO_4.7H_2O$	10.5	7.5	42.0	19.0	
W	Leonite	Kainite	$MgSO_4.7H_2O$	9.0	7.5	45.0	19.5	
X	$MgSO_4.6H_2O$	Kainite	$MgSO_4.7H_2O$	3.5	4.0	65.5	13.0	
Y	$MgSO_4.6H_2O$	Kainite	Kieserite	1.5	2.0	77.0	10.0	
Z	Carnallite	$MgCl_2.6H_2O$	Kieserite	1.0	0.5	100.0	5.0	

Graphic Representation.—The data given in Table XVI, *A*, are graphically represented in the diagram, Fig. 7 (Van't Hoff). The several fields circumscribed in this diagram represent the following mineral bodies:

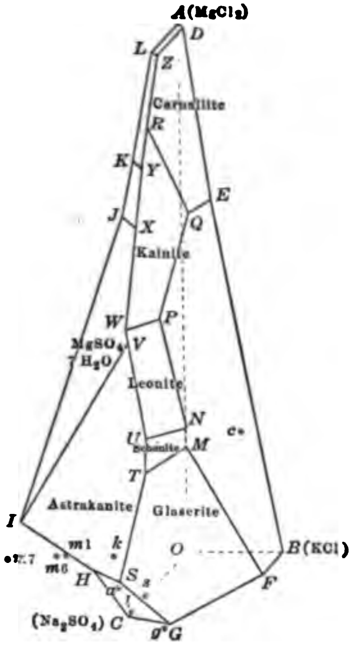

FIG. 7.—Saturation diagram for salts in presence of NaCl at 25°C. (*Redrawn after Van't Hoff.*) For significance of letters see Table XVI *A*.

Field	Mineral body	Composition
1. A-L-Z-D	Bischofite	$MgCl_2.6H_2O$
2. B-F-M-N-P-Q-E	Sylvite (Sylvine)	KCl
3. C-G-S-H	Thenardite	Na_2SO_4
4. D-Z-R-Q-E	Carnallite	$MgKCl_3.6H_2O$
5. F-M-T-S-G	Glaserite	$K_4Na_2(SO_4)_3$
6. S-H-I-V-U-T	Astrakanite	$Na_2Mg(SO_4)_2.4H_2O$
7. J-X-W-V-I	Reichardtite	$MgSO_4.7H_2O$
8. J-X-Y-K	Not found in nature	$MgSO_4.6H_2O$
9. K-Y-R-Z-L	Kieserite	$MgSO_4.H_2O$
10. T-U-N-M	Schönite	$MgK_2(SO_4)_2.6H_2O$
11. N-U-V-W-P	Leonite	Mg(1.5K, 0.5Na) $(SO_4)_2.4H_2O$
12. P-W-X-Y-R-Q	Kainite	$MgSO_4.KCl.3H_2O$

Paragenesis of the Minerals.—The paragenesis or simultaneous development of the several minerals at 25°C. is illustrated in the diagram by the lateral junctions of the fields. All of the 12 mineral species[1] may appear with rock salt (NaCl), but some of the others can not appear simultaneously at this temperature. Thus it is seen, that the combination Astrakanite and Kainite is not possible at 25°C.—the fields do not adjoin. But Astrakanite may appear with Reichardtite, Leonite, Schönite, Glaserite and Thenardite. This is even better expressed in the rectangular diagram (Fig. 8) which clearly indicates the paragenesis of the several mineral species at this temperature.

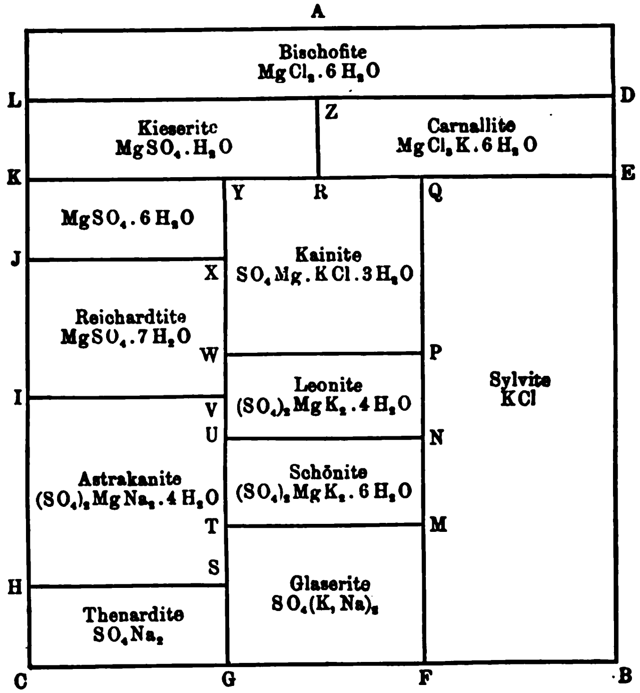

FIG. 8.—Diagram illustrating the paragenesis of oceanic salts at 25°C. (*Van't Hoff.*)

In the next Table, XVI, *B*, the composition of the solution saturated for sodium chloride and other salts (mother-liquor type) at the crystallization points is given.

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[1] One of these (No. 8) is unknown in a state of nature.

TABLE XVI, *B*.—COMPOSITION OF SOLUTION SATURATED FOR SODIUM CHLORIDE AND OTHER SALTS IN EQUILIBRIUM AT 83°C.

	Saturated for NaCl and			1,000 mol. H_2O in mol.				
				Na_2Cl_2	K_2Cl_2	$MgCl_2$	$MgSO_4$	Na_2SO_4
O	....	....	....	59.0				
A	$MgCl_2.6H_2O$	....	....	1.0	....	121.0		
B	KCl	....	....	39.0	37.0			
C	Na_2SO_4	....	....	56.5	....	....	.....	8.0
D	$MgCl_2.6H_2O$	Carnallite	....	1.0	2.0	117.0		
E	KCl	Carnallite	....	1.5	10.0	92.0		
F	KCl	Glaserite	....	39.5	39.0	....	.....	4.5
G	Na_2SO_4	Glaserite	....	43.5	21.0	....	.....	11.5
H	Na_2SO_4	Vanthoffite	....	51.0	....	4.5	10.5	
I	Vanthoffite	Loeweite	....	35.0	....	22.0	12.5	
K	Loeweite	Kieserite	....	18.0	....	45.0	11.0	
L	Kieserite	$MgCl_2.6H_2O$	....	1.0	....	120.0	1.0	
P	KCl	Glaserite	Langbeinite	29.5	33.5	13.0	10.0	
Q	KCl	Carnallite	Kieserite	2.0	12.0	86.5	5.0	
R	KCl	Langbeinite	Kieserite	11.0	15.0	76.0	5.0	
S	Glaserite	Na_2SO_4	Vanthoffite	43.0	22.5	....	7.5	5.5
V	Loeweite	Glaserite	Vanthoffite	34.5	26.5	8.5	17.5	
W	Loeweite	Glaserite	Langbeinite	30.0	24.5	12.0	16.5	
Y	Loeweite	Kieserite	Langbeinite	16.0	10.5	42.0	14.0	
Z	Carnallite	$MgCl_2.6H_2O$	Kieserite	1.0	2.0	116.0	1.0	

Graphic Representation.—The data given in Table XVI, *B*, are graphically presented in the diagram, Fig. 9 (Van't Hoff) and from this it is seen, that at 83°C. only 9 mineral species are represented in addition to the rock salt (NaCl). These are the following:

Field	Mineral species	Composition
1. A-L-Z-D	Bischofite	$MgCl_2.6H_2O$
2. B-F-P-R-Q-E	Sylvite	KCl
3. C-G-S-H	Thenardite	Na_2SO_4
4. D-Z-Q-E	Carnallite	$MgKCl_3.6H_2O$
5. F-P-W-V-S-G	Glaserite	$(KNa)_2SO_4$
9. K-Y-R-Q-Z-L	Kieserite	$MgSO_4.H_2O$
13. K-Y-W-V-I	Loeweite	$Mg_2Na_4(SO_4)_4.5H_2O$
14. I-V-S-H	Vanthoffite	$MgNa_6(SO_4)_4$
15. W-P-R-Y	Langbeinite	$Mg_2K_2(SO_4)_3$

Paragenesis of the Mineral Species.—The simultaneous occurrence of the mineral species at 83°C. is shown by the junction of the several fields in the diagram, and this is again better shown in the rectangular diagram, Fig. 10*b*. It will be seen, that the formation of half of the mineral species (6–8, 10–12) is no longer

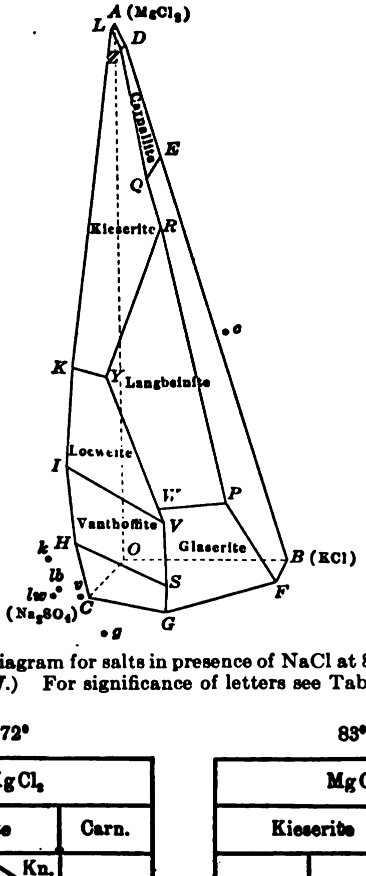
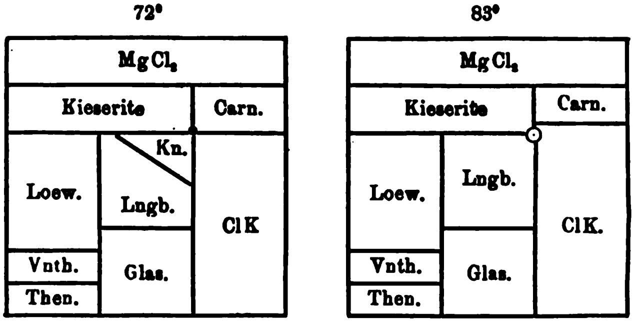


FIG. 9.—Saturation diagram for salts in presence of NaCl at 83°C. (*Redrawn after Van't Hoff.*) For significance of letters see Table XVI *B*.



a *b*

FIG. 10.—Diagrams showing paragenesis of oceanic salts at 72° and 83°C. (*Van't Hoff.*)

possible at this temperature, these being Schönite (No. 10) which falls away at 26°C., Reichardtite (No. 7) at 31°C., Magnesium sulfathexahydrate (No. 8) at 35.5°C., Astrakanite (No. 6) at 60°C., Leonite (No. 11), at 61.5°C., and Kainite (No. 12) at 83°C. The diagram, Fig. 10*a*, shows that all of these except Kainite (Kn) have disappeared at 72°C., this last disappearing rapidly. At the same time the formation of three new minerals (13–15) becomes possible, namely: Langbeinite (No. 15) at 37°C., Loeweite (No. 13) at 43°C., and Vanthoffite (No. 14) at 46°C. With this falling away of older, and appearance of newer mineral species, corresponding changes in the paragenesis of the other minerals becomes possible. Thus at 25°C. the paragenesis of Leonite and Glaserite was not possible (see Fig. 8) but with the disappearance of Schönite at 26°C. this becomes possible. These changes are expressed in a series of diagrams given by Van't Hoff to which the student is referred.[1]

Application of These Principles.—The studies of Van't Hoff and his associates have shown, that the formation, at 25°C. (77°F.) and at 83°C. (184.4°F.), of the following double salts, which occur as natural mineral species in the salt deposits of Stassfurt (see Chap. XXIV), and other regions, is possible with the solutions given in the following table.

TABLE XVII.—FORMATION OF DOUBLE SALTS

Mineral species	Composition	Mols. in 1,000 mols. H_2O						Temperature	
		NaCl	KCl	$MgCl_2$	Na_2SO_4	K_2SO_4	$MgSO_4$	C.	F.
Carnallite	$MgCl_2.KCl.6H_2O$	....	6	89	....	....	....	25	77.0
Schönite	$MgSO_4.K_2SO_4.6H_2O$	....	....	....	....	11	40	25	77.0
Glaserite	$3K_2SO_4.Na_2SO_4$	88	30	....	9	....	....	25	77.0
Kainite	$MgSO_4.KCl.3H_2O$	11	12	61	....	....	12	25	77.0
Leonite	$2MgSO_4.K_2SO_4.4H_2O$	24	20	40	....	....	17	25	77.0
Astrakanite	$Na_2SO_4.MgSO_4.4H_2O$	75	....	2	....	....	27	25	77.0
Langbeinite	$2MgSO_4.K_2SO_4$	43	42	36	....	....	11	83	181.4
Loeweite	$2MgSO_4.2Na_2SO_4.5H_2O$	53	....	34	....	....	12	83	181.4
Vanthoffite	$MgSO_4.3Na_2SO_4$	86	....	13	....	....	12	83	181.4

Order of Separation at 25°C.—With sea water of the following composition in molecules per one thousand molecules of water $1{,}000H_2O$, $24NaCl$, $15.5KCl$, $40.7MgCl_2$, $20MgSO_4$, which is the condition of saturation for the salts in question when all of them are present in the water, Van't Hoff finds the following order of separation of the salts, always in company with sodium chloride:

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[1] Zur Bildung der ozeanischen Salzablagerungen. Braunschweig, 1915, Figs. 17–27.

1. Magnesium sulphate.
2. Magnesium sulphate and Kainite.
3. Hexahydrate and Kainite.
4. Kieserite and Kainite.
5. Kieserite and Carnallite.
6. Kieserite, Carnallite, Magnesium chloride.

From sea water condensed until it is saturated for sodium chloride (but not for the other salts) with the composition in molecules 1,000H_2O, 100NaCl, 2.2KCl, 7.8$MgCl_2$, 3.8$MgSO_4$, the following four stages of salt separation are deducible at 25°C.:

1. *Older Rock Salt,* separation of NaCl until the solution becomes 1,000H_2O, 24NaCl, 11.5KCl, 40.7$MgCl_2$, 20$MgSO_4$.
2. *Kieserite region,* separation of sodium chloride, magnesium sulphate and Kainite until the solution becomes 1,000 H_2O, 2NaCl, 2KCl, 85.5$MgCl_2$, 8$MgSO_4$.
3. *Carnallite region,* separation of sodium chloride, Carnallite, and Kieserite until the solution becomes 1,000H_2O, 2 NaCl, 1KCl, 100$MgCl_2$, 5$MgSO_4$.
4. *Final Mother Liquor,* what remains in the solution solidifies in the following proportions: 0.15NaCl, 7.62$MgCl_2$, 0.08 Carnallite, 0.38Kieserite.

These steps are summarized in the following table given by Van't Hoff.

TABLE XVIII.—ORDER AND PROPORTIONS OF SEPARATION OF SALT MINERALS AT 25°C. FROM SEA WATER OF NORMAL PROPORTIONS 1,000H_2O, 100NaCl, 2.2KCl, 7.8$MgCl_2$, 3.8$MgSO_4$.

	Rock Salt	Kieserite	Kainite	Carnallite	Bischofite
1........	95.4				
2........	4.42	1.05	2.02		
3........	0.03	0.35	....	0.10	
4........	0.15	0.38	....	0.08	7.62
	100.00 NaCl	1.78	2.02	0.18	7.62
		3.8 $MgSO_4$		2.2 KCl	7.8 $MgCl_2$

Order of Separation at 83°C.—If normal ocean water (1,000 molecules H_2O, 100NaCl, 2.2KCl, 7.8$MgCl_2$, 3.8$MgSO_4$) is condensed at 83°C. (181.4°F.), the separation of sodium chloride is followed by that of Loeweite ($MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$) at a composition of the solution of the following proportions:

$1,000H_2O, 29.7Na_2Cl_2, 7.6KCl, 26.9MgCl_2, 13.1MgSO_4$

After this follows successively Kieserite, Carnallite and Bischofite, always in company with sodium chloride.

Thus both at 25°C. and 83°C. the primary products from sea water include: (1) Kieserite, (2) Carnallite, (3) Bischofite, a succession entirely in harmony with that found in natural salt deposits.

Temperature Conditions for the Paragenesis of the Salt Minerals

In the paragenesis or the simultaneous development of the several salt minerals, temperature forms a very important factor. In the following table from Van't Hoff, the temperatures at which the several minerals form, either directly, or as secondary products (meta-salts, which see) are given. The minus sign (−) indicates that the paragenesis does not take place between 25° and 83°C. The plus sign (+) indicates that the paragenesis is possible throughout the entire range of that temperature interval.

Natural temperatures rising above 70°C. (158°F.) have been found in the deeper layers of the waters of salt lakes, where the heat from the sun's rays appears to be imprisoned by the strong brines.

Gypsum and Anhydrite Deposits from Sea Water.—The separation of calcium sulphate from sea water involves essentially the problem of the conditions favoring separation of anhydrite and those favoring the separation of gypsum. As these processes are in operation in desert deposits as well, their consideration will be deferred to a later section. (See pp. 176–179.)

TABLE XIX.—TEMPERATURE RANGES IN PARAGENESIS OF SALT MINERALS BETWEEN TEMPERATURES 25° AND 83° (VAN'T HOFF)

	Langbeinite	Vanthoffite	$MgSO_4.6H_2O$	Carnallite	Leonite	Glaserite	Sylvite	Kainite	Kieserite	Astrakanite	
Thenardite	–	above 46	–	–	–	+	–	–	–	to 49	
$MgSO_4.7H_2O$	–	–	to 31	–	to 28	–	–	to 27	–	to 31	
Schönite	–	–	–	–	to 26	to 26	to 26	–	–	to 26	
Loeweit	ab. 43	ab. 60	–	–	47 to 62	ab. 57	–	–	ab. 43	43 to 60	
Astrakanite	38 to 47	46 to 60	28 to 36	–	to 57	to 60	–	–	32 to 49		
Kieserite	ab. 37	–	to 36	+	32 to 38	–	ab. 72	to 83			
Kainite	37 to 83	–	to 32	to 72	to 55	–	to 83				
KCl (Sylvite)	ab. 55	–	–	+	to 61	+					
Glaserite	ab. 61	ab. 46	–	–	26 to 62						
Leonite	37 to 62	–	27 to 32	–							

CHAPTER IV

CONDITION OF DEPOSITION OF SEA SALTS IN NATURE

Salts may be abstracted from ocean water in a number of ways, among which the following may be considered as the most important:

A. By Organic Agencies—Organic Salts (Bioliths).

B. By reaction with other salts or with liquids or gases introduced—Precipitation Salts (Precipitates).

C. By concentration of the water—Concentration Salts (Evaporates).

D. By atmospheric distribution—Cyclic Salts.

Of these, the first method is the most important in the open sea, the second much less so, while the third is commoner in marginal lagoons and salt pans. Cyclic salts are rare and confined to the coastal belt.

To these may be added the separation of a certain quantity of sea water from the ocean by enclosure within the pores of the sediments. Salt water and additional salts thus abstracted become connate waters and salts, and they may be liberated again from the rocks after these have been lifted above the sea. These salts are discussed in connection with other salts of continental origin in a later chapter.

A. ORGANIC SEA SALTS

These consist mainly of carbonate of lime in the form of calcite or aragonite. To a lesser degree silica is deposited by a certain group of organisms. Precipitation is generally upon and within the tissues of the organism by chemical reaction, and a definite structure and, commonly, external form is given to the deposit which is easily recognized under proper conditions.

The lime-secreting or lime-precipitating organisms in the sea are both plants and animals.

Lime Salts Secreted by Marine Plants

Bacteria.—These, by effecting decay in organic matter, produce ammonium carbonate, which reacts with the calcium salts of the sea water to precipitate calcium carbonate. Denitrifying bacteria, especially the form known as *Pseudomonis calcis* (Fig. 11) cause abundant precipitation of lime in the warmer waters of the tropics. This lime is largely in the form of oölite. In their researches, Kellerman and Smith have succeeded in producing deposits of calcium carbonate in the laboratory in the following manner: By the associative action of mixed cultures of bacteria, one species which forms traces of carbon dioxide and one which forms ammonia either by decomposing some proteid or by reducing nitrates to nitrites and to ammonia. In this manner ammonium carbonate is produced, which reacts with calcium sulphate as follows: $CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4$. The carbon dioxide may also be produced by plant or animal catabolism, as well as by bacterial fermentation. Calcium carbonate may also be precipitated from water carrying calcium bicarbonate by bacterial production of ammonia $(Ca(HCO_3)_2 + 2NH_4QH = CaCO_3 + (NH_4)_2CO_3 + H_2O$. Calcium carbonate may also be precipitated as a result of bacterial decomposition of calcium salts of organic acids, such as calcium succinate, calcium acetate, or calcium nitrate.[1]

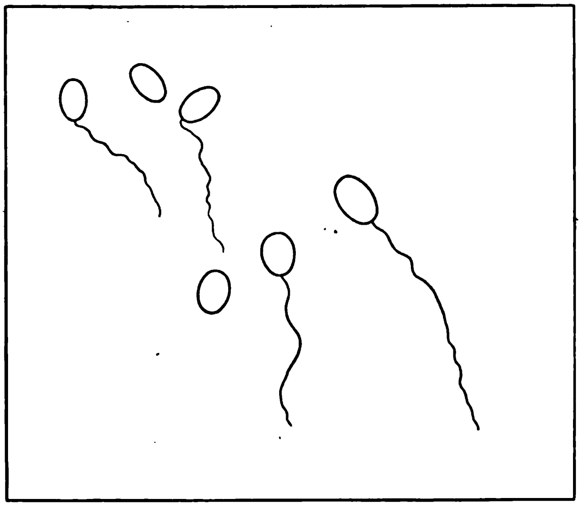

FIG. 11.—Pseudomonis calcis (much enlarged).

Algæ.—Numerous marine algæ secrete lime within or upon the outer cells of their tissues, and so build up a strong and often extensive stony deposit of lime. They are classed together as *Nullipores*, and their significance in the building of reef rocks in the ocean is very great. Large deposits of older limestones are also chiefly due to them. Modern examples are: *Corallina* (Fig. 12), *Lithothamnum* (Fig. 13), and *Halimeda* (Fig. 14). A fresh water form is *Chara* (Fig. 15), which is an important limestone maker. A peculiar marine pelagic form is represented by the coccoliths (coccolithophora) (Fig. 16).

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[1] Karl F. Kellerman and N. R. Smith, Bacterial Precipitation of Calcium Carbonate, Jour. Wash. Acad. Sci., Vol. IV, No. 14, pp. 400–402, 1914. George Harold Drew, On the Precipitation of Calcium Carbonate in the Sea by Marine Bacteria, or On the Action of Denitrifying Bacteria in Tropical and Temperate Seas. Publ. No. 182, Carnegie Inst. of Washington, pp. 7–45, 1914.

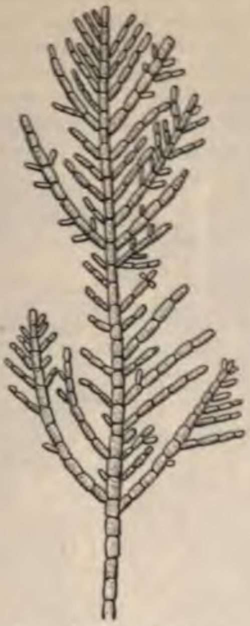

FIG. 12.—Corallina sp.

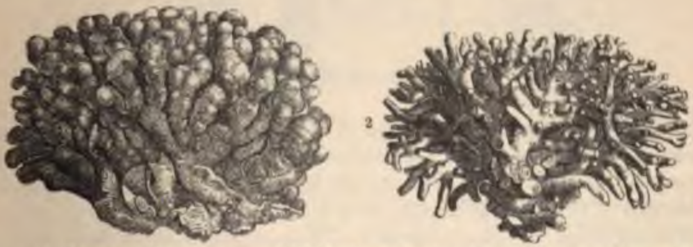

FIG. 13.—Two modern species of Lithothamnium, a lime-secreting alga, playing an important part in the making of coral reefs. Isle Maurice. (*After Zittel.*)

Lime Salts Secreted by Marine Animals

Nearly all classes of marine animals secrete lime in the form of calcite or aragonite, to build their protective or supporting structures. Marine vertebrates also secrete lime phosphate in their bones and teeth.

Foraminifera.—These build an external shell of calcite in one group (Vitro-calcarea) and of aragonite in another (most porcellanous ones). Of the former *Globigerina* (Fig. 17) is an example of the latter *Peneroplis* (Fig. 18). An older foraminiferal rock is represented by the chalk (Fig. 19).

Sponges.—Only a small group of these, the *Calcarea*, build structures composed of calcareous rods and networks (Fig. 20) the so-called spicules. The material is probably always calcite.

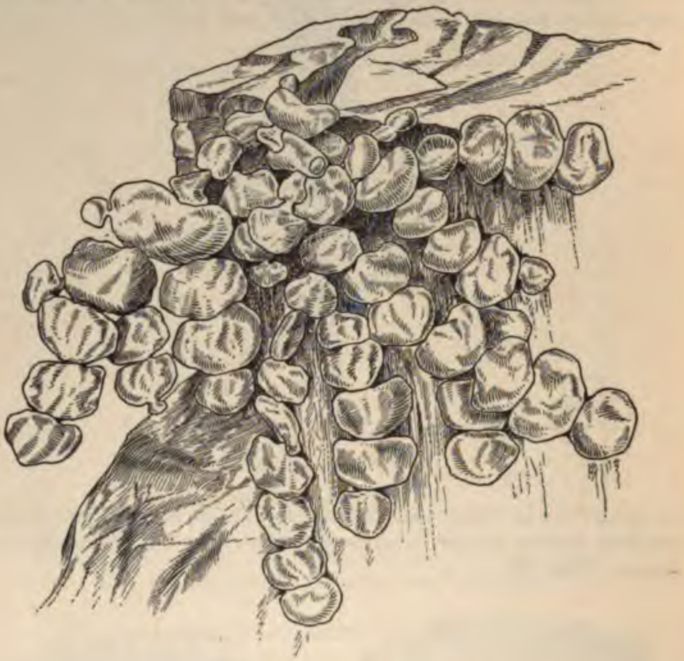

Fig. 14.—Halimeda tuna.

Corals and Hydrocorallines (Figs. 21 to 28, pp. 85–89).—These build structures which in some forms are calcite and in others aragonite. They are among the chief limestone producers in the seas of all ages. In many forms carbonate of magnesia is present in moderate quantity.

Bryozoa (Figs. 29, 30, pp. 89–90).—These animals build coral-like uctures, often of great importance as limestone makers, especially in the past. The lime is mostly in the form of calcite.

Brachiopods (Figs. 31, 32, pp. 91–92).—These build shells of lime in the form of calcite. They are of vast importance as limestone makers in some geological periods.

Mollusca (Figs. 33 to 38, pp. 93–97).—Thesealso build chiefly external shells of lime which is mostly in the form of aragonite though in every class

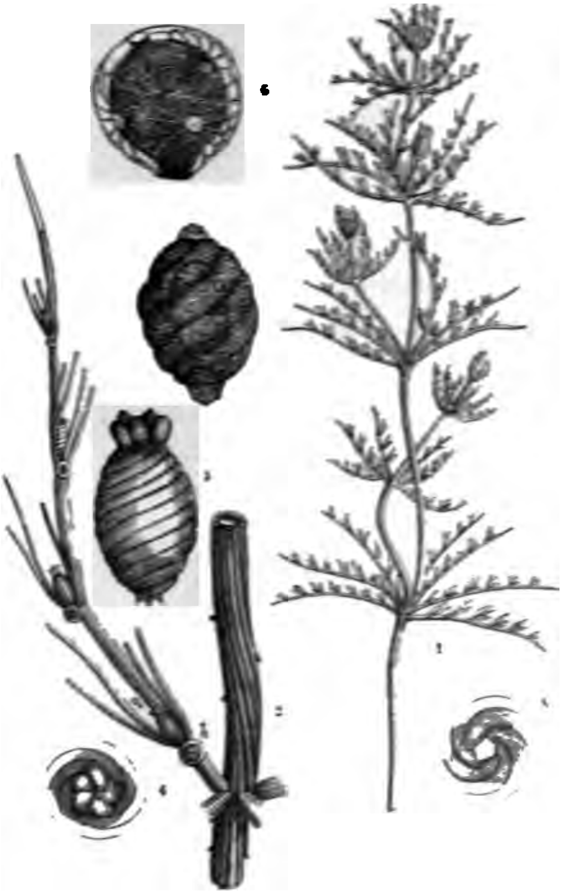

FIG. 15.—*Chara vulgaris* L. A fresh-water alga which precipitates calcium carbonate upon its surface and is an important source of marl and fresh-water limestone. 1. Complete plant. 2. Fragment with sporangia and antheridia (enlarged). 3. Sporangium much enlarged. 4. Summit of a sporangium after fall of the crown. 5. Basal portion of a sporangium. 6 & 7. Antheridia and sporangium of another form (*Nitella flexilis* Ag.). Much enlarged. (After *Zittel*.)

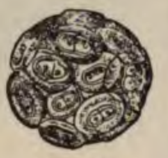

FIG. 16.

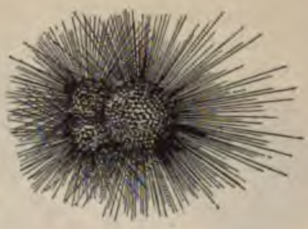

FIG. 17.

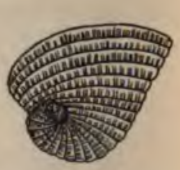

FIG. 18.

FIG. 16.—A coccolithophore or floating marine organism, referred to the algæ, which secretes oval plates of calcium carbonate. These plates form an important part of deep sea oozes. They also occur in chalk. Greatly enlarged. (*After Murray.*)

FIG. 17.—*Globigernia.* A modern genus of Foraminifera, floating in the upper oceanic waters. The figure shows the many-chambered shell, pierced by holes or foramina, through which the fleshy threads or pseudopodia project. The shells form the chief component of the deep sea globigernia ooze. Much enlarged. (*After Murray.*)

FIG. 18.—*Peneroplis*, a modern foraminifer shell with external pores only on the upper surface of the last elongated chambers. Other pores connect the successive chambers. Mostly in shallow water.

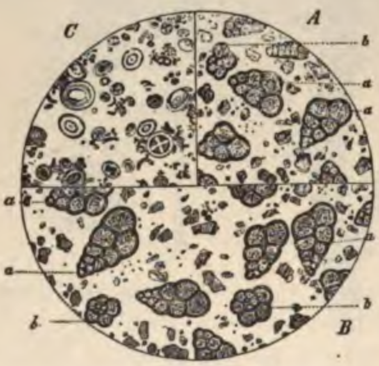

FIG. 19.

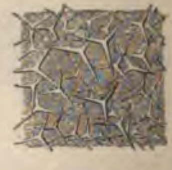

FIG. 20.

FIG. 19.—Thin sections of chalk. *A*. White chalk from Sussex, England. *B*. Chalk from Farafrah, Libyan desert. Both enlarged 60 diameters. Two species of foraminiferal shells are prominent in each. *a. Textularia globulosa* *b. Rotalia* (*Discorbina*) *marginata*. C. Dried residue of milky chalk water with coccoliths. Enlarged 700 diameters. (*After Zittel.*)

FIG. 20.—Triradiate spicules of a modern calcareous sponge. Enlarged about 50 times. (*After Zittel.*)

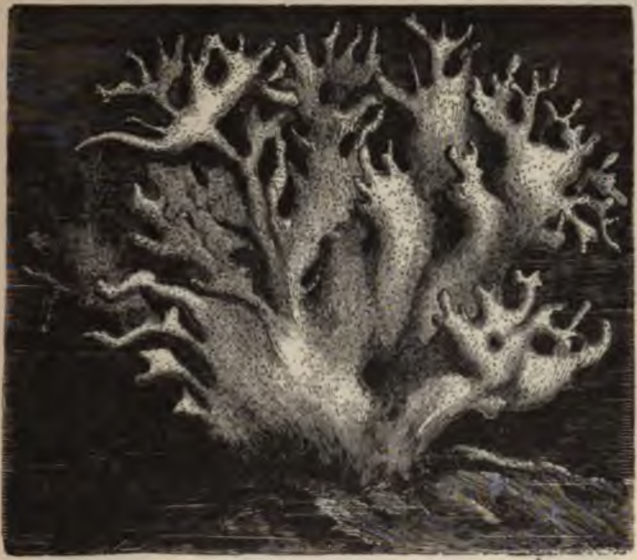

FIG. 21.—A modern hydrocoralline (*Millepora alcicornis*). An important reefbuilder. (*After Dana Corals and Coral Islands, by permission of Dodd Mead & Co.*)

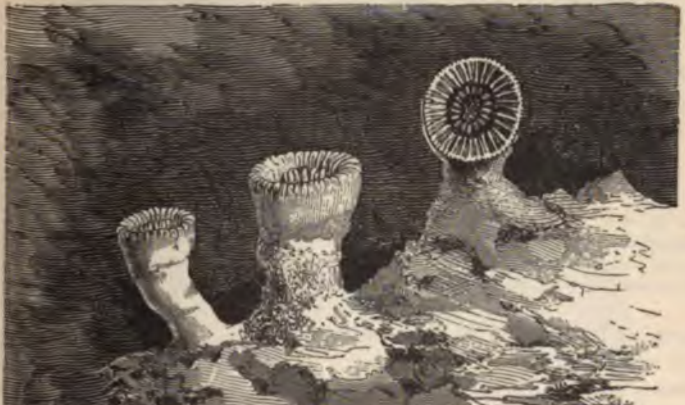

FIG. 22.—A modern simple or cup coral (*Caryophyllia cyathus*). Attached to sea bottom. (*After Dana Corals and Coral Islands, by permission of Dodd Mead & Co.*)

there are some that build shells of calcite like the Pecten, Oyster and others. Some bivalve mollusks or pelecypods (Fig. 33) build their shells with an outer layer of calcite and an inner one of aragonite, as in the case of the common salt water mussel *Mytilus* and the fresh water bivalve *Unio*. The same is true for some of the gastropods as well (Fig. 34). A few of the cephalopods (Figs. 35, 36), especially *Argonauta* and the extinct Belemnite build a structure of calcite, but most of the shells of this class are aragonite (Ammonites (Fig. 37, p. 96)). Pteropods (Fig. 38, p. 97) have generally a shell of aragonite.

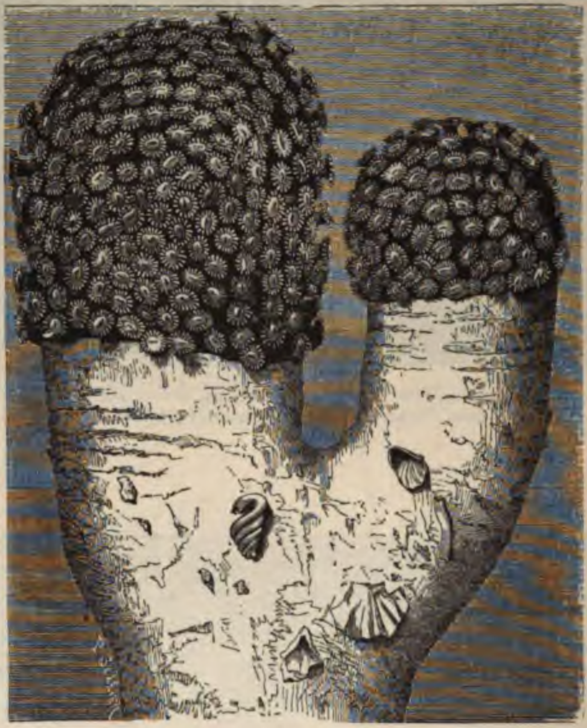

FIG. 23.—A modern compound coral. *Goniopora columna D.* The ends of the branches are covered by the living animals or polyps. The lower part is dead and frequently overgrown with foreign matter. (*After Dana, Corals and Coral Islands, by permission of Dodd Mead & Co.*)

Crustacea (Figs. 39–41).—The larger members of this division as a rule build shells of organic material only partly impregnated with lime in the form of calcite. (Crabs, Trilobites (Fig. 39, p. 97)). Some forms build shells or other structures entirely of calcite (Ostracods (Fig. 40, p. 98), Barnacles (Fig. 41, p. 98), etc.).

Echinoderms (Figs. 42–44).—These build structures composed of numerous closely joined or loosely disposed plates, all of which are of calcite. In the

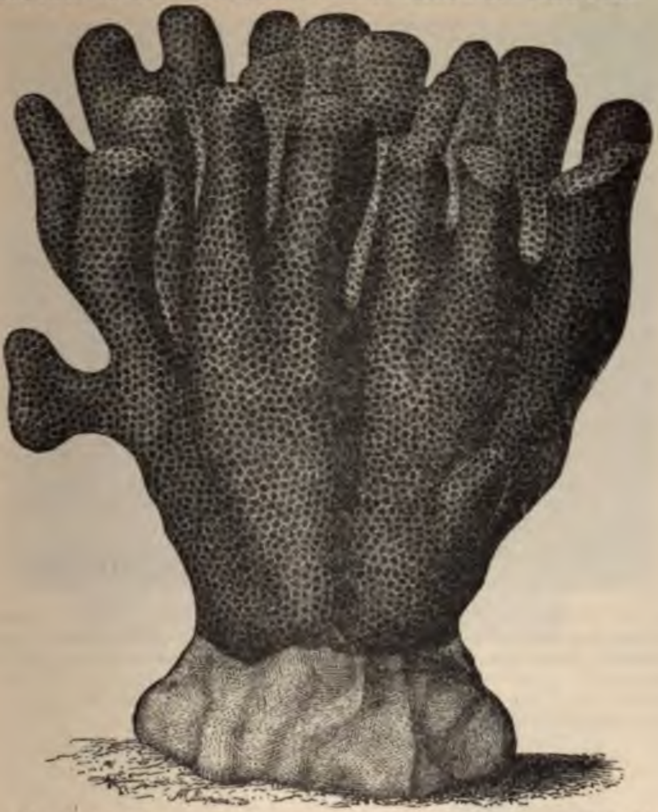

FIG. 24.—A modern coral stock with many branches (*Porites mordax* D.). An important reef builder. The polyps are small and closely crowded. (*After Dana, Corals and Coral Islands, by permission of Dodd Mead & Co.*)

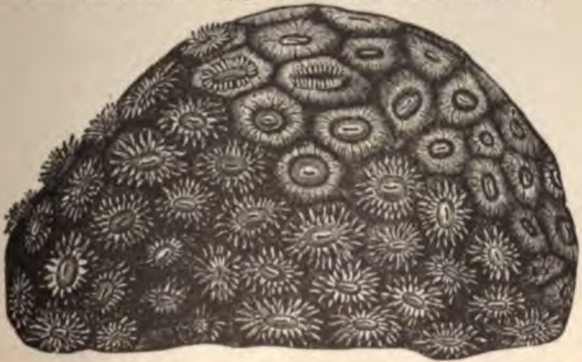

FIG. 25.—A modern head of coral. (*Astræa pallida* Dana.) The polyps are large and crowded and so assume a pentagonal or hexagonal form. Half of their number is shown expanded, with tentacles surrounding the mouth; the others are contracted. (*After Dana, Corals and Coral Islands, by permission of Dodd Mead & Co.*)

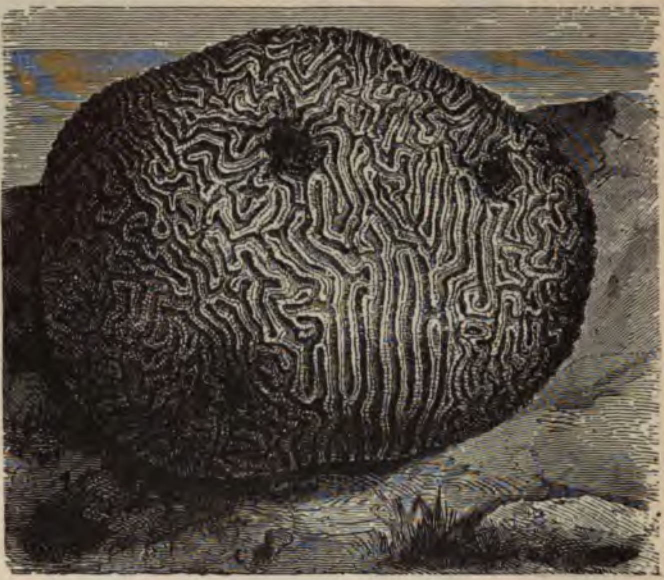

FIG. 26.—A modern Brain coral (*Diploria cerebriformis*, E & H). The small polyps are disposed in winding rows separated by strong parallel ridges, strongly convoluted. (*After Dana, Corals and Coral Islands, by permission of Dodd Mead & Co.*)

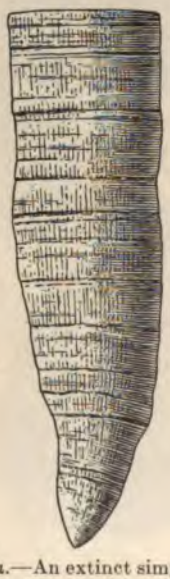

FIG. 27*a*.—An extinct simple or cup coral (*Streptelasma rusticum*) from the upper Ordovicic of the Cincinnati region.

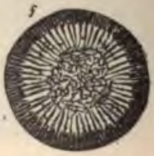

FIG. 27*b*.—A cross-section of the coral shown in Fig. 27*a*, showing the septa twisted at the center.

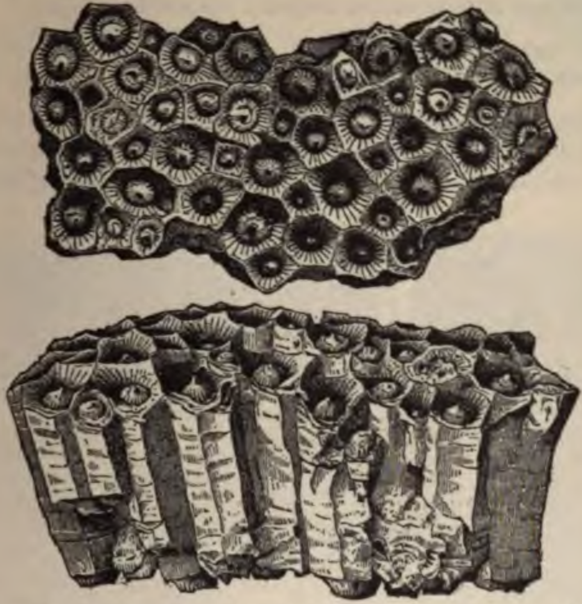

FIG. 28.—An extinct compound coral (*Lithostrotion mamillare*). Mississippic limestones of North America. The corallites are prismatic from crowding. The center of each is elevated tent-like with a rod, the columella projecting beyond. (*From Grabau & Shimer, N. Am. Index Fossils.*)

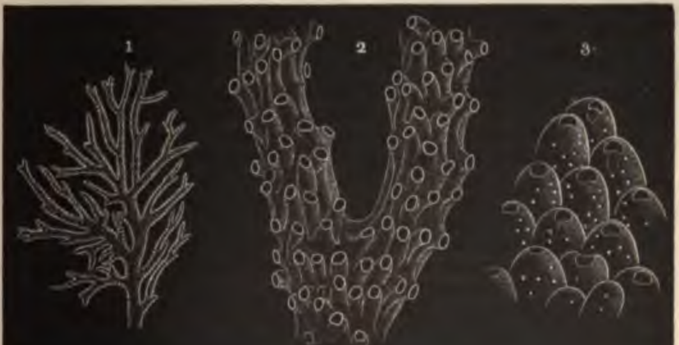

FIG. 29.—A group of modern Bryozoa. 1. *Hornera lichenoides*, natural size. 2. Portion of same enlarged. 3. *Discopora skenei* Smitt, portion enlarged. (*From Dana, Corals and Coral Islands, by permission of Dodd Mead & Co.*)

skeletons of one of the classes, the crinoids (Figs. 42, 43, p. 100), a considerable amount of carbonate of magnesia has also been found.

Worms.—Some marine worms build calcareous tubes which add to the general mass of lime accumulation on the sea-bottom (Fig. 45, p. 101).

Phosphate of lime is secreted by a few brachiopods (*Lingula*, Fig. 100, p. 308) and by the vertebrates (fish, whales, etc.), the bones of which contain about 40 per cent. of phosphoric acid.

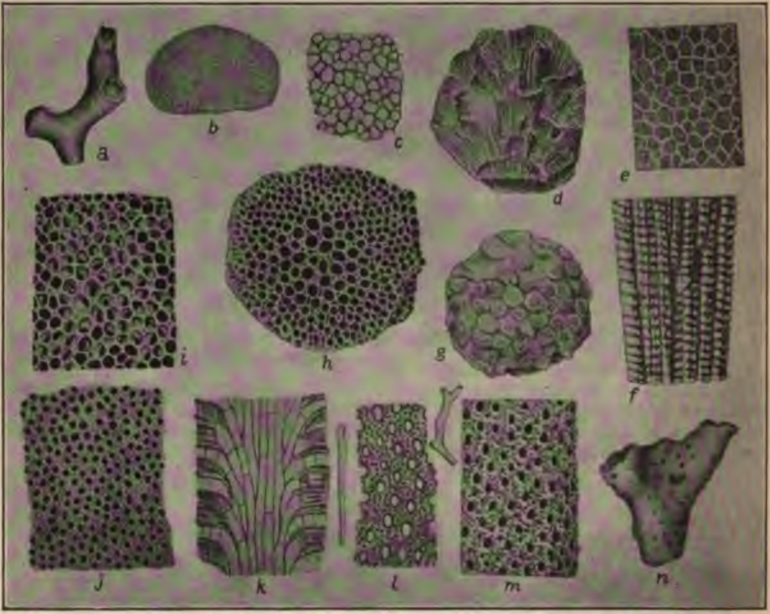

FIG. 30.—Rock building Bryozoa of former geological periods. (*After Grabau and Shimer, North American Index Fossils.*) a, *Batostoma winchelli;* (Ordovicic). b, c, *Ceriopora micropora,* complete mass and enlargement of surface; (Eocenic). d, e, f, *Monotripa tabutata,* fragment, enlarged tangential section and enlargement of tubes; (L. Devonic); g, h, *Aspidopora elegantula,* entire head, and enlarged monticule (U. Ordovicic); i, *Hemiphragma tenuimurale* enlargement of surface (U. Ordovicic); j, *Nicholsonella pulchra,* enlargement of surface (M. Ordovicic); k, l, m, *Batostomella spinulosa,* vertical and tangential sections, outline of form (small) and surface enlarged (Mississippic); n, *Dekayella prænuntia* var *echinata.* (M. Ordovicic.)

Silica Secreted by Marine Plants

Silica is secreted by a much smaller number of marine organisms. It is generally an isotropic, glassy form of silica containing some water. The following forms are noteworthy:

Among marine plants, only the pelagic diatoms (Fig. 46, p. 102) secrete a siliceous structure. This has the form of capsules, often of considerable variety and beauty. They form extensive deposits on some portions of the ocean bottom.

Silica Secreted by Marine Animals

Radiolaria (Fig. 47, p. 102).—This class builds for the most part a siliceous structure of very variable form. Vast areas of the deeper portions of the ocean bottom are covered by these capsules.

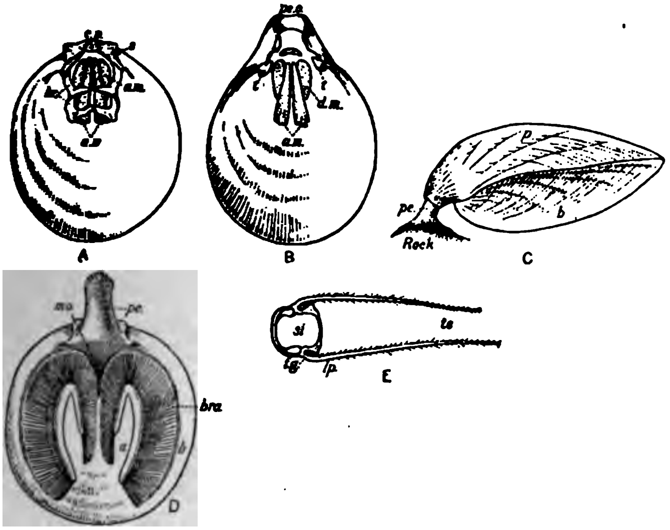

Fig. 31.—A modern Brachiopod (*Terebratulina septentrionalis*). *A*. Inside of brachial valve showing the hinge apparatus, the arm supports (brachidia) *br* and the muscle scars. *B*. Interior of pedicle valve showing the muscle scars, (*dm*, *am*), the hinge teeth *t*, and the pedicle opening *pe.o*. *C*. Entire shell with valves closed, attached by pedicle (*pe*) to rock, the normal mode of growth. *D*. The soft body of the animal, with pedicle valve removed. *E*. Cross-section of arm or brachium along line *ab* in Fig. *D*. Much enlarged. (*From Shimer's Introduction to the Study of Fossils, by permission of The MacMillan Co.*)

Sponges (Figs. 48, p. 103).—A large group of living and extinct sponges build structures of siliceous spicules. These are the most prolific source of organic silica found in flints and cherts in marine limestones.

Other Salts Secreted by Organisms

Potash and Iodine Secreted by Marine Algæ.—Marine algæ, especially the larger brown algæ found along our coasts, separate salts from the sea water and store them in their tissues. Potash and iodine are among the most important of the elements thus included in the plant tissue, and algæ are a not unimportant source of these valuable substances. The most noteworthy of these algæ are the Giant Kelps of the Pacific Coasts, among which the following have recently attracted the attention of seekers after potash salts:[1]

Macrocystis pyrifera (Fig. 49, p. 104).—This kelp has a stem or stipe growing generally from 90 to 100 feet in length, while a length of 1,000 feet has been reported. Several stipes arise from a "hold fast" or root-like expansion, each stipe bearing at intervals along its entire length a series of fronds or leaves, each of which has at its base a small air bladder or *pneumatocyst*, which is roughly pear-shaped and about 2 inches long by 1 inch at its widest section. Each frond averages 12 to 14 inches in length, and 3 to 4 inches in width at its widest part, and is serrated along its margins. This kelp grows in groves several miles in length, and from 50 to 100 yards up to 2 miles or more in width. It lives in 3 to 10 fathoms of water and may be cut safely at a depth of 2 fathoms, since the spores develop on the fronds at considerable

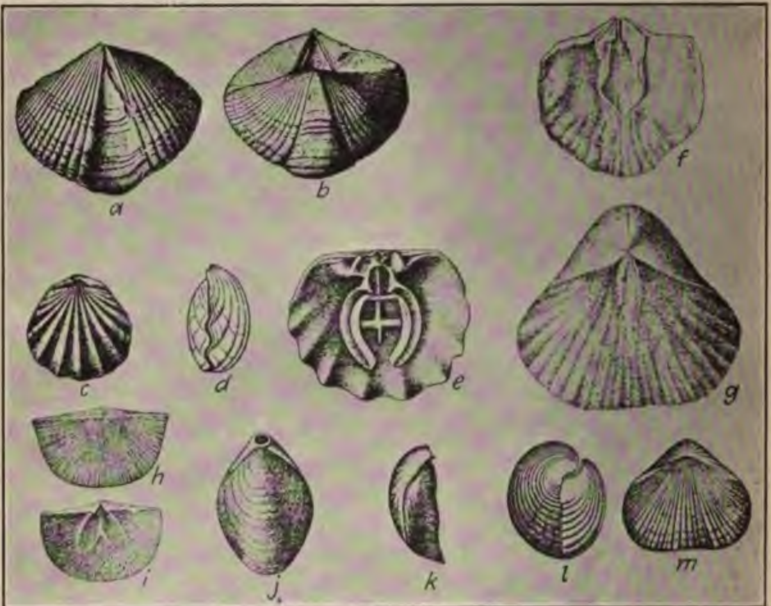

FIG. 32.—Fossil Brachiopoda. *a, b. Spirifer fornacula*, Hall, Devonic; *c, d*, *Terebratella plicata* (Say); *e*, interior of brachial valve enlarged, Cretacic; *f, g*, *Gypidula romingeri* H. & Cl., Devonic; *h, i*, *Plectambonites sericeus* (Sowerby), Ordovicic; *j, k*, *Terebratulina atlantica* (Morton) Cretacic; *l, m*, *Anastrophia verneuili* (Hall), Lower Devonic. (*After Grabau & Shimer, North American Index Fossils.*)

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[1] Frank K. Cameron, Potash from Kelp, U. S. Dept. Agriculture, Report No. 100, 1915, with portfolio of maps. See also, John S. Burd. The Economic Value of Pacific Coast Kelps; College of Agriculture, Experiment Station, Berkeley, Cal., Bull. 249, 1915.

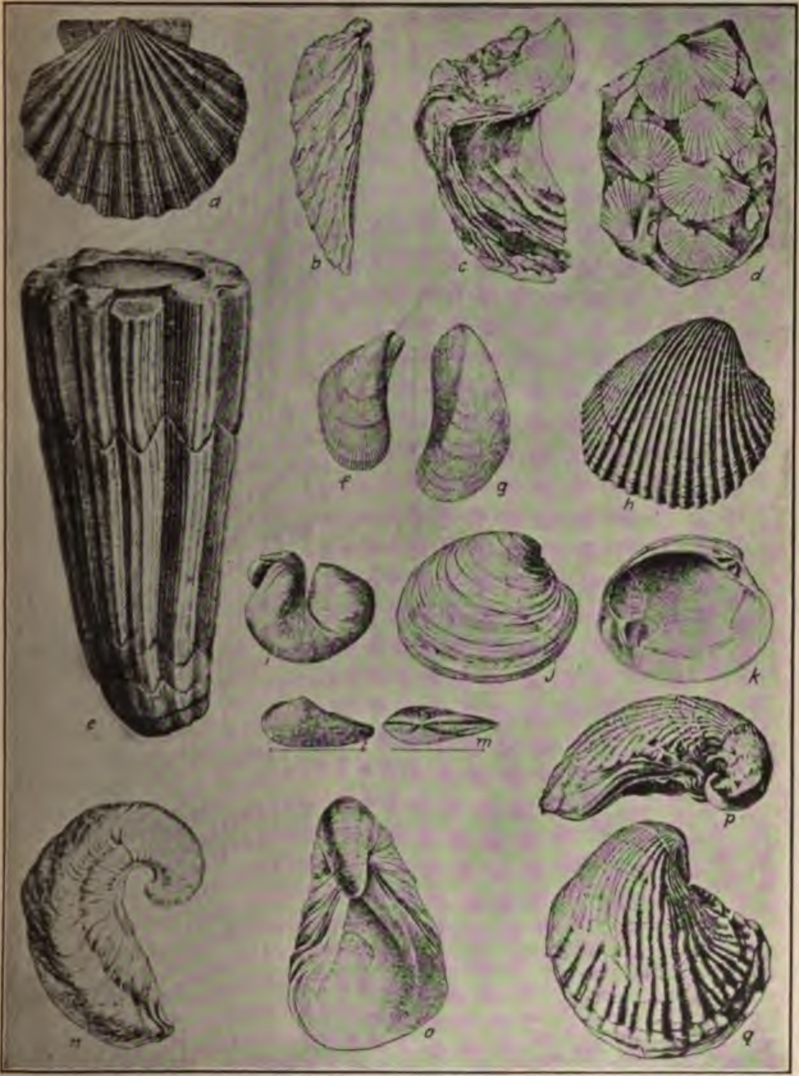


Fig. 33.—Fossil Pelecypoda. *a*, *Pecten madisonius*, Say, Miocenic; *b*, *c*, *Ostrea sellæformis*, Conrad, Eocenic; *d*, *Daonella lommeli*, Wiss. Triassic; *e*, *Radiolites texanus*, Roemer, Comanchic; *f*, *Modiola alabamensis*, Ald., Eocenic; *g*, *M. multilinigera*, Meek, Cretacic; *h*, *Venericardia smithi* Aldr., Eocenic; *i*, *Requienia patagiata*, White, Comanchic; *j*, *k*, *Venus mercenaria* L. Miocenic-Recent; *l*, *m*, *Leda bellistriata*, Stevens, Miss.–Permic; *n*, *o*, *Gryphæa mucronata*, Gabb, Comanchic; *p*, *q*, *Exogyra costata*, Say, Cretacic. (Mostly reduced.) (*After Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

depth below the surface. The species is probably perennial and has a life history certainly longer than a year.

Its distribution is reported from Sitka southward throughout the west coast of America. On the east coast it ranges from the southern end of South America to latitude 43° S. For analysis of its ash, see Table XX.

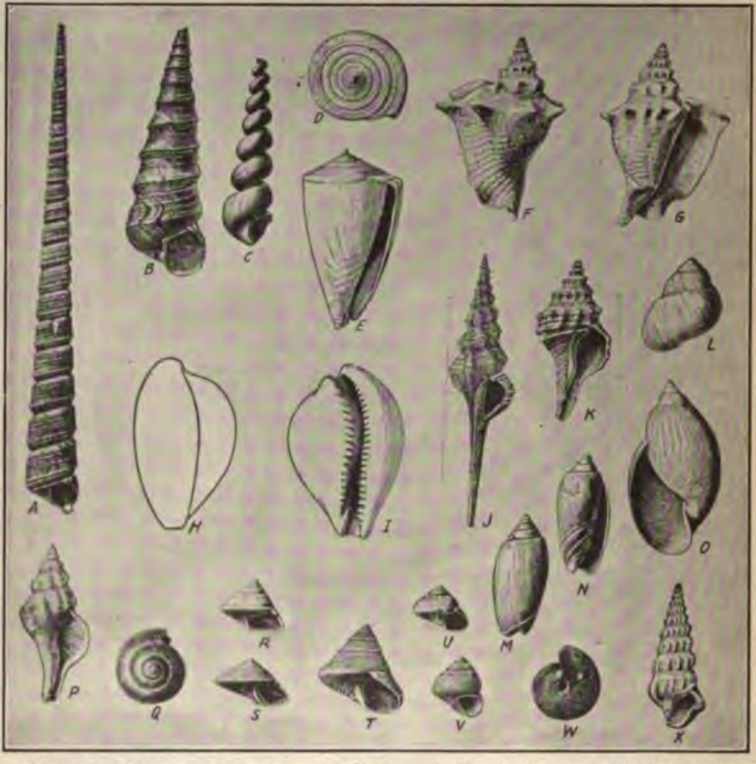


FIG. 34.—Types of Gastropod Shells. *A, Turritella cumberlandia* Conrad, Miocenic; *B, C, Turritella mortoni* Conrad, shell and internal mold, Eocenic; *D, E. Conus planiceps*, Dall, summit and side view, Oligocenic; *F, G, Strombus chipolanus*, Dall, Oligocenic; *H, I, Cypræa pinguis* Conrad, Eocenic–Miocenic; *J, Falsifusus meyeri* (Aldr.), Eocenic; K, *Urosalpinx strumosa* (Conrad), Miocenic; *L, Viviparus leai*, M & H, Cretacic; *M, N, Oliva literata* Lam. Miocenic-Recent; *O, Physa meigsii*, Dall, Pliocenic; *P, Lathyrus floridanus*, Heilpr., Eoc.-Mioc.; *Q, S, W, Calliostoma humele* (Conr.), Miocenic; *R, C. eboreum* (Wagner), Miocenic; *T, C. philanthropus* (Conr.) Miocenic; *U, C. aphelium*, Miocenic; *V, Gibbula glandula* (Conr.), Eocenic; *X, Potamides scalatus*, Heilpr., Pliocenic. (Mostly reduced.) *(From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.)*

Alaria fistulosa (Fig. 50, p. 104).—This is a much smaller form with a stipe only about 8 inches long and ending in a "hold fast." From this arises a bunch of relatively small leaves, which are spore producers. From this bunch proceeds a long, rather fragile leaf, averaging 40 feet in length, and with an average width of less than 20 inches, but ranging up to 5 feet in some

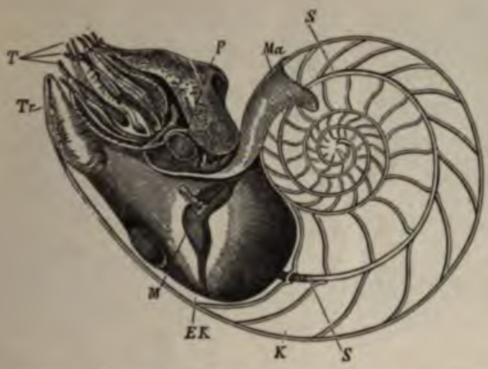


FIG. 35.—Nautilus. A living shelled cephalopod animal, with shell sectioned through median plane. *T.* Tentacles. *P.* Eye. *Ma.* Dorsal flaps of mantle. *Tr.* Funnel or hyponome. *M.* Adductor muscle. *S.* Siphon. *EK.* Living chamber. *K.* Air chambers. (*After Felix, Leitfossilien.*)

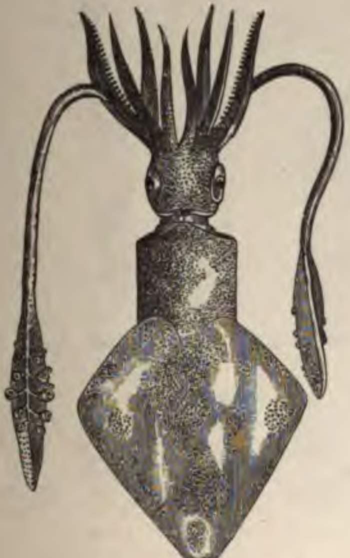
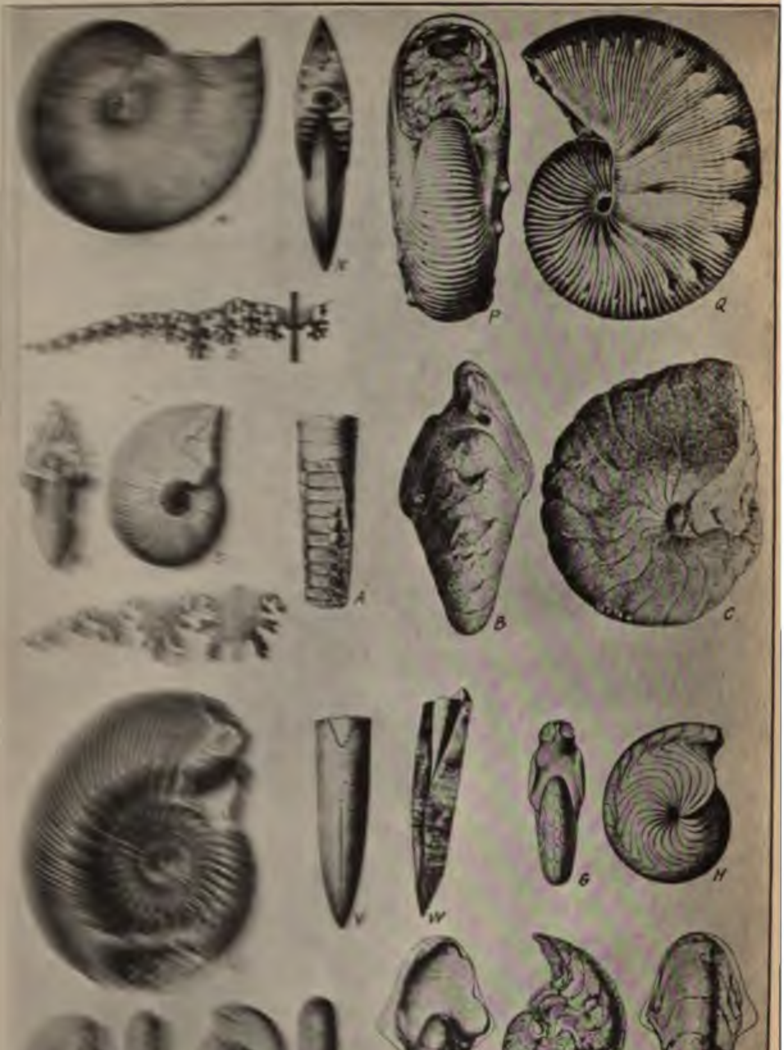


FIG. 36.—The modern squid (*Loligo vulgaris*). A living cephalopod with internal horny shell-remnant. Relative of the Belemnite. (*After Felix, Leitfossilien.*)



[illegible] Cephalopod Shells. A, *Orthoceras* (*Loxoceras*) *monitiforme* [illegible] *Hercoglossa*), *tuomei* Clark & Martin; Eocenic; [illegible] (White), Eocenic; *O*, *H*, *Goniatites* (*Aga-* [illegible] Mississippic; *I*, *J*, *Goniatites* (*Muensteroceras*) *parallelum* [illegible] (*Muensteroceras*) *oweni* (Hall), Mississippic; *M*, *N*, *O*, [illegible] (Owen), with suture; Cretacic; *P*, *Q*, *Scaph-* [illegible] Cretacic; *R*, *S*, *T*, *Ammonites* (*Cardioceras*) *cordi-* [illegible] Jurassic; *U*, *Ammonites* (*Olcostephanus*) *loganianus* [illegible] *V*, *W*, *Belemnites densus*, guard and section of same, [illegible] Jurassic. (All reduced.) (*After Grabau and* [illegible] *Fossils*, A. G. Seiler & Co.)

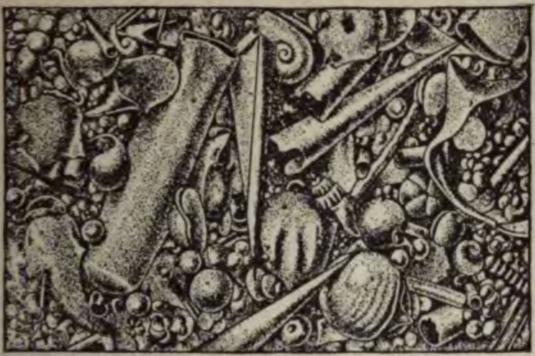


FIG. 38.—A mass of Pteropod shells from a deep sea pteropod ooze. Enlarged 10 diameters. (*After Murray and Renard.*)

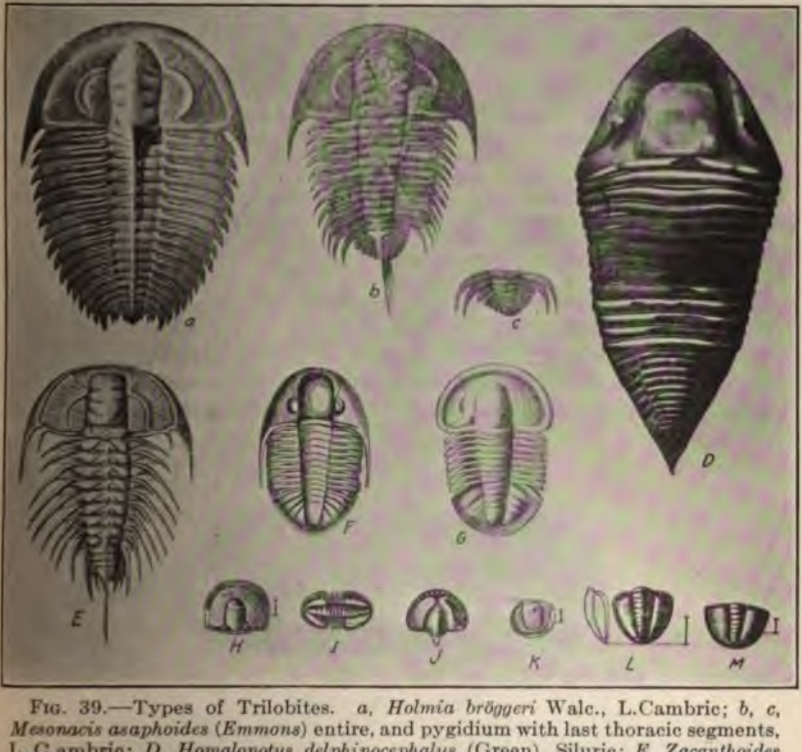


FIG. 39.—Types of Trilobites. *a, Holmia bröggeri* Walc., L.Cambric; *b, c, Mesonacis asaphoides* (*Emmons*) entire, and pygidium with last thoracic segments, L. Cambric; *D, Homalonotus delphinocephalus* (Green), Siluric; *E, Zacanthoides typicalis* Walc., M. Cambric; *F, Bathyurus extans* Hall, Ordovicic; *G, Asaphiscus wheeleri* Meek, M. Cambric; *H, K, Microdiscus acadicus* Hartt, M. Cambric; *I, Microdiscus speciosus* Ford; *L*, pygidium enlarged, L. Cambric; *J, M, Microdiscus pulchellus*, Hartt, M. Cambric. (*A-G*, reduced.) (*After Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

[illegible] The leaf has a hollow, flattened mid-rib perhaps an inch in [illegible] intervals of a few inches, at which points the tube [illegible] closed to form a series of floats. The growth is in the [illegible] which must not be cut.

[illegible] Types of Ostracoda. *A, Primitia seminulum* Jones, ×12, [illegible] (Ulrich), ×7, Devonic; *C, D, Aechmina abnormis* [illegible] *crassinoda* (Ulrich), ×7, Ordovicic; *G, H, I,* [illegible] dorsal, lateral (left) and posterior views ×13, [illegible] Jones, dorsal view, ×13, Cretacic (fresh [illegible] Jones, lateral and dorsal views, ×13, Cretacic [illegible] Jones, lateral and dorsal views, ×13, [illegible] *angulifera*, Whitf. Siluric; *R, S, Primi-* [illegible] Devonic. (*From Grabau and Shimer, North* [illegible] & Co.)

[illegible] abounds in the tideways along the Alaskan [illegible] see Table XX.

[illegible] Fig. 32, p. 104).—This form has a length of stipe of [illegible] and shorter. It terminates on one end in a [illegible] 7 or 8 inches in external diameter, and with

[illegible] to a stone. (*Balanus pictis.*) Mio-[illegible] (*After Zittel.*)

[illegible] The lower end of the stipe ends in a [illegible] the stipe spring several long, string-[illegible] initial leaf.

[illegible] is more commonly found in the tide-[illegible] and propagates itself by means of spores [illegible] the leaves. For analysis of ash, see [illegible]

Pelagophycus porra.—This species probably contains more potash than the other three, but it occurs scattered on the seaward edge of the Macrocystis beds in quantities too small to be of importance.

Analyses of the ash of the three principal kelps dried in an oven at 105°C. gave the following results.

TABLE XX.—ANALYSES OF ASHES FROM KELP. ASH DRIED AT 105°C.[1]

	1 Macrocystis pyrifera	2 Alaria fistulosa	3 Nereocystis luetkeana
Average of number of analyses.....	58	15	51
Total soluble salts, per cent	30.0	24.4	46.9
Potash (K_2O).....................	12.59	9.1	20.1
Iodine (I).........................	1.57	Trace	0.13
Nitrogen (N).....................	....	2.6	1.9
Ash..............................	5.9	7.5	4.2
Range of Potash (K_2O), per cent.	....	2.9 to 13.1	6.58 to 31.62
Range of Nitrogen (N), per cent.	....	2.1 to 3.3	0.81 to 3.06

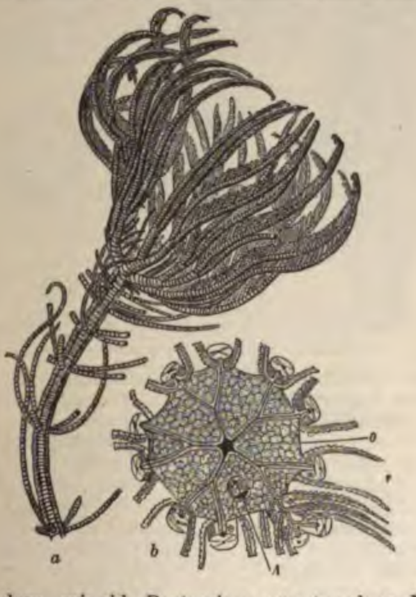


FIG. 42.—A modern crinoid *Pentacrinus caput-medusæ* Müller. *a.* Calyx with arms and part of stem. *b.* Oral surface enlarged showing central mouth (*o*) and eccentric anus (*A*). (*After J. Müller, from Felix Leitfossilien.*)

The production of potash (K_2O) from kelp in the United States in 1916 was 1,556 short tons, valued at the point of shipment at

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[1] For many detailed analyses see Burd, *loc. cit.*

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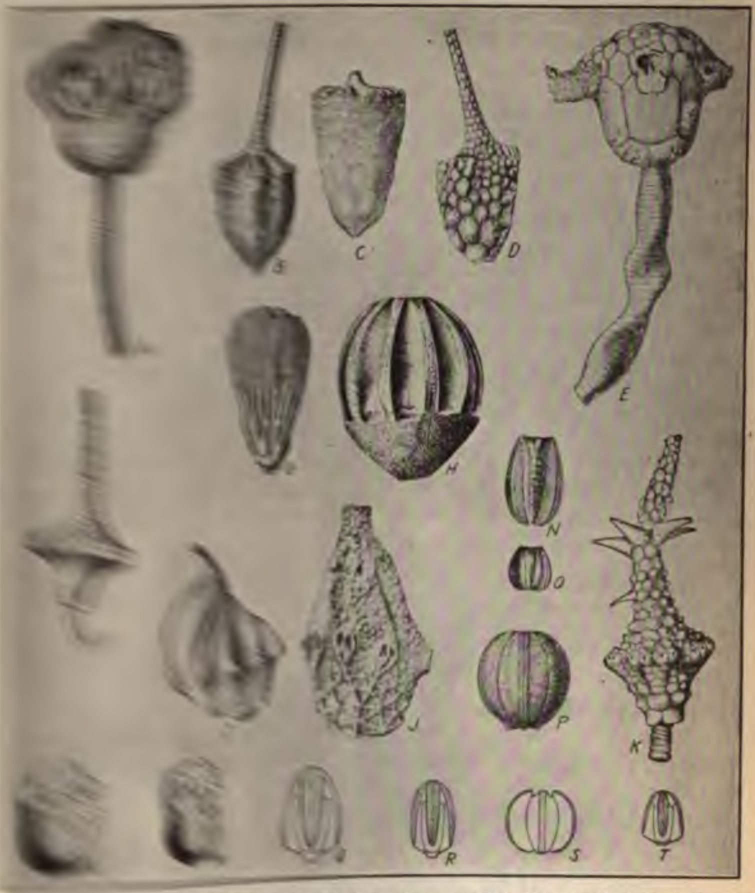


[illegible] A, *Megistocrinus nobilis* W. & S. Mississippic; [illegible] Hall, Siluric; C, *P. tennesseensis* (Hall), Siluric; E, [illegible] Mississippic; F, *Eutrochocrinus christyi* (Shumard), [illegible] *aequalis* (Hall), Mississippic; H, *Eucalyptocrinus* [illegible] Siluric; I, J, *Siphonocrinus nobilis* (Hall), internal mold, and [illegible] *nashvillae* (Troost), Mississippic; L, M, *Carabo-* [illegible] Ordovicic. Fossil Blastoids: N, O, *Elæacrinus elegans* [illegible] N, part of one side, nat. size, Devonic; P, *Elæacrinus* [illegible] S. & G., × ½, Devonic; Q, R, *Pentremites elongatus* (Shu- [illegible] Mississippic; S, *Granatocrinus norwoodi*, O. & S. Mississ- [illegible] (Hall), Mississippic. (All reduced, N & O [illegible] and Shimer, *North American Index Fossils*, A. G. Seiler secrete a siliceous structure. This has the form of capsules, often of considerable variety and beauty. They form extensive deposits on some portions of the ocean bottom.

Silica Secreted by Marine Animals

Radiolaria (Fig. 47, p. 102).—This class builds for the most part a siliceous structure of very variable form. Vast areas of the deeper portions of the ocean bottom are covered by these capsules.

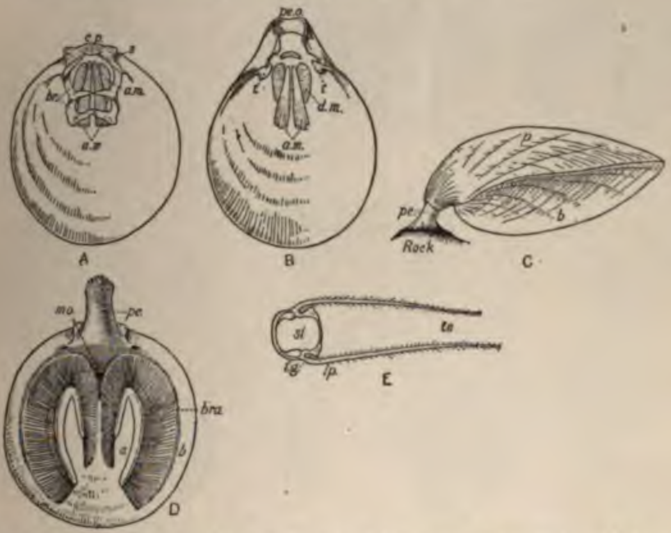


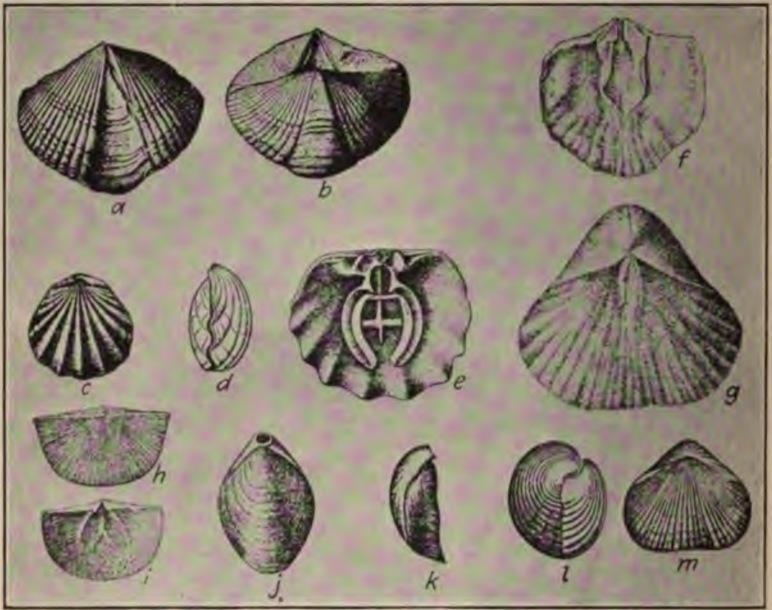
Fig. 31.—A modern Brachiopod (*Terebratulina septentrionalis*). *A*. Inside of brachial valve showing the hinge apparatus, the arm supports (brachidia) *br* and the muscle scars. *B*. Interior of pedicle valve showing the muscle scars, (*dm*, *am*), the hinge teeth *t*, and the pedicle opening *pe.o*. *C*. Entire shell with valves closed, attached by pedicle (*pe*) to rock, the normal mode of growth. *D*. The soft body of the animal, with pedicle valve removed. *E*. Cross-section of arm or brachium along line *ab* in Fig. *D*. Much enlarged. (*From Shimer's Introduction to the Study of Fossils, by permission of The MacMillan Co.*)

Sponges (Figs. 48, p. 103).—A large group of living and extinct sponges build structures of siliceous spicules. These are the most prolific source of organic silica found in flints and cherts in marine limestones.

Other Salts Secreted by Organisms

Potash and Iodine Secreted by Marine Algæ.—Marine algæ, especially the larger brown algæ found along our coasts, separate salts from the sea water and store them in their tissues. Potash and iodine are among the most important of the elements thus included in the plant tissue, and algæ are a not unimportant source of these valuable substances. The most noteworthy of these algæ are the Giant Kelps of the Pacific Coasts, among which the following have recently attracted the attention of seekers after potash salts:[1]

Macrocystis pyrifera (Fig. 49, p. 104).—This kelp has a stem or stipe growing generally from 90 to 100 feet in length, while a length of 1,000 feet has been reported. Several stipes arise from a "hold fast" or root-like expansion, each stipe bearing at intervals along its entire length a series of fronds or leaves, each of which has at its base a small air bladder or *pneumatocyst*, which is roughly pear-shaped and about 2 inches long by 1 inch at its widest section. Each frond averages 12 to 14 inches in length, and 3 to 4 inches in width at its widest part, and is serrated along its margins. This kelp grows in groves several miles in length, and from 50 to 100 yards up to 2 miles or more in width. It lives in 3 to 10 fathoms of water and may be cut safely at a depth of 2 fathoms, since the spores develop on the fronds at considerable



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[1] Frank K. Cameron, Potash from Kelp, U. S. Dept. Agriculture, Report No. 100, 1915, with portfolio of maps. See also, John S. Burd. The Economic Value of Pacific Coast Kelps; College of Agriculture, Experiment Station, Berkeley, Cal., Bull. 249, 1915.

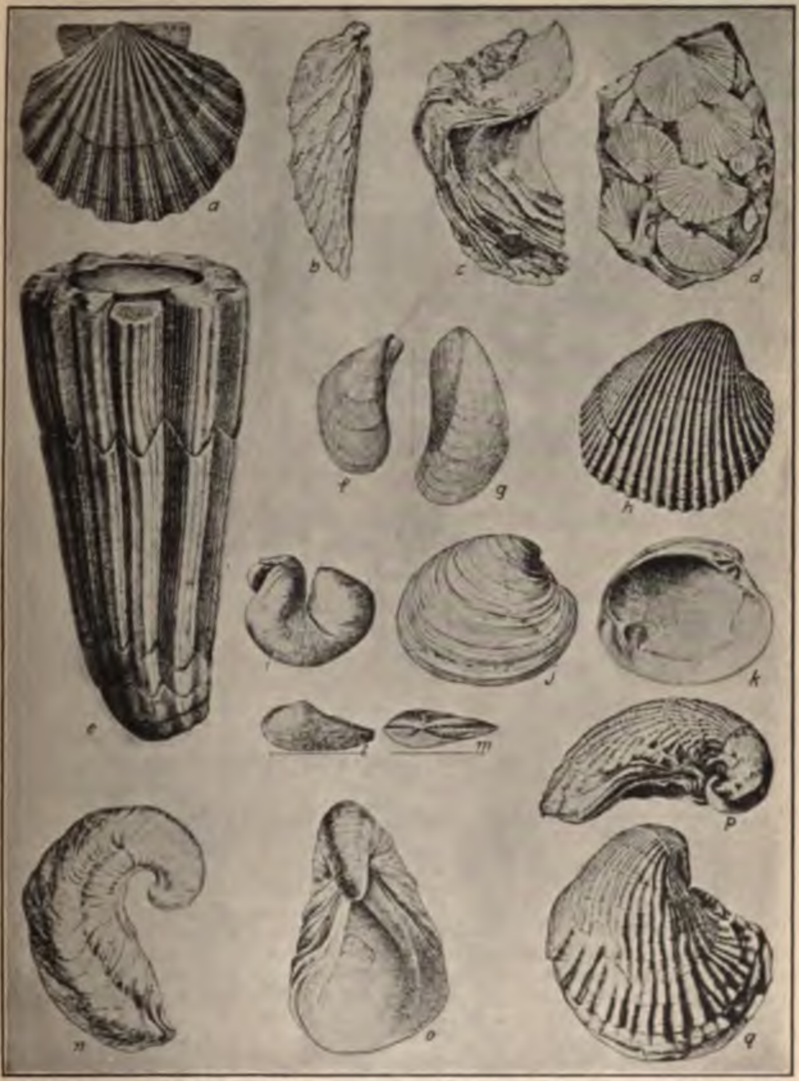

FIG. 33.—Fossil Pelecypoda. *a*, *Pecten madisonius*, Say, Miocenic; *b*, *c*, *Ostrea sellæformis*, Conrad, Eocenic; *d*, *Daonella lommeli*, Wiss. Triassic; *e*, *Radiolites texanus*, Roemer, Comanchic; *f*, *Modiola alabamensis*, Ald., Eocenic; *g*, *M. multilinigera*, Meek, Cretacic; *h*, *Venericardia smithi* Aldr., Eocenic; *i*, *Requienia patagiata*, White, Comanchic; *j*, *k*, *Venus mercenaria* L. Miocenic-Recent; *l*, *m*, *Leda bellistriata*, Stevens, Miss.-Permic; *n*, *o*, *Gryphæa mucronata*, Gabb, Comanchic; *p*, *q*, *Exogyra costata*, Say, Cretacic. (Mostly reduced.) (*After Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

depth below the surface. The species is probably perennial and has a life history certainly longer than a year.

Its distribution is reported from Sitka southward throughout the west coast of America. On the east coast it ranges from the southern end of South America to latitude 43° S. For analysis of its ash, see Table XX.

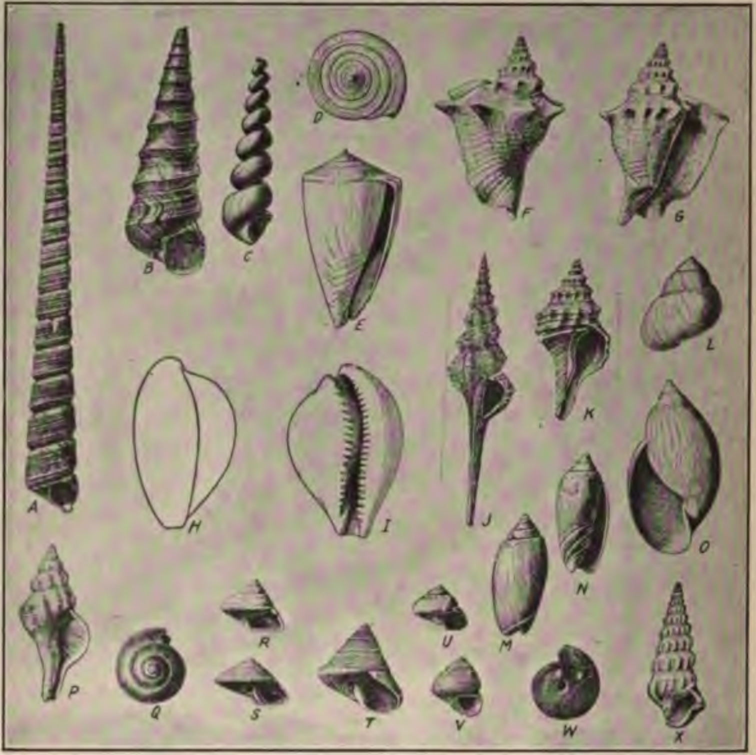

Fig. 34.—Types of Gastropod Shells. *A*, *Turritella cumberlandia* Conrad, Miocenic; *B*, *C*, *Turritella mortoni* Conrad, shell and internal mold, Eocenic; *D*, *E*, *Conus planiceps*, Dall, summit and side view, Oligocenic; *F*, *G*, *Strombus chipolanus*, Dall, Oligocenic; *H*, *I*, *Cypræa pinguis* Conrad, Eocenic–Miocenic; *J*, *Falsifusus meyeri* (Aldr.), Eocenic; K, *Urosalpinx strumosa* (Conrad), Miocenic; *L*, *Viviparus leai*, M & H, Cretácic; *M*, *N*, *Oliva literata* Lam. Miocenic-Recent; *O*, *Physa meigsii*, Dall, Pliocenic; *P*, *Lathyrus floridanus*, Heilpr., Eoc.-Mioc.; *Q*, *S*, *W*, *Calliostoma humele* (Conr.), Miocenic; *R*, *C. eboreum* (Wagner), Miocenic; *T*, *C. philanthropus* (Conr.) Miocenic; *U*, *C. aphelium*, Miocenic; *V*, *Gibbula glandula* (Conr.), Eocenic; *X*, *Potamides scalatus*, Heilpr., Pliocenic. (Mostly reduced.) (*From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

Alaria fistulosa (Fig. 50, p. 104).—This is a much smaller form with a stipe only about 8 inches long and ending in a "hold fast." From this arises a bunch of relatively small leaves, which are spore producers. From this bunch proceeds a long, rather fragile leaf, averaging 40 feet in length, and with an average width of less than 20 inches, but ranging up to 5 feet in some

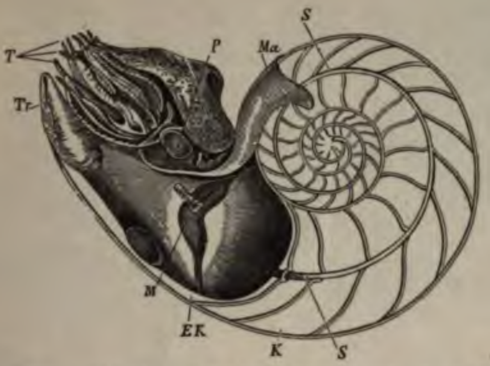

FIG. 35.—Nautilus. A living shelled cephalopod animal, with shell sectioned through median plane. *T*. Tentacles. *P*. Eye. *Ma*. Dorsal flaps of mantle. *Tr*. Funnel or hyponome. *M*. Adductor muscle. *S*. Siphon. *EK*. Living chamber. *K*. Air chambers. (*After Felix, Leitfossilien.*)

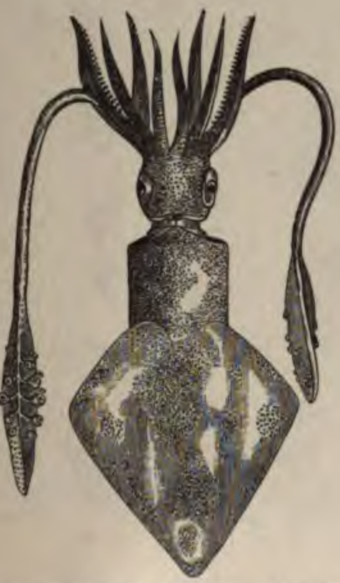

FIG. 36.—The modern squid (*Loligo vulgaris*). A living cephalopod with internal horny shell-remnant. Relative of the Belemnite. (*After Felix, Leitfossilien.*)

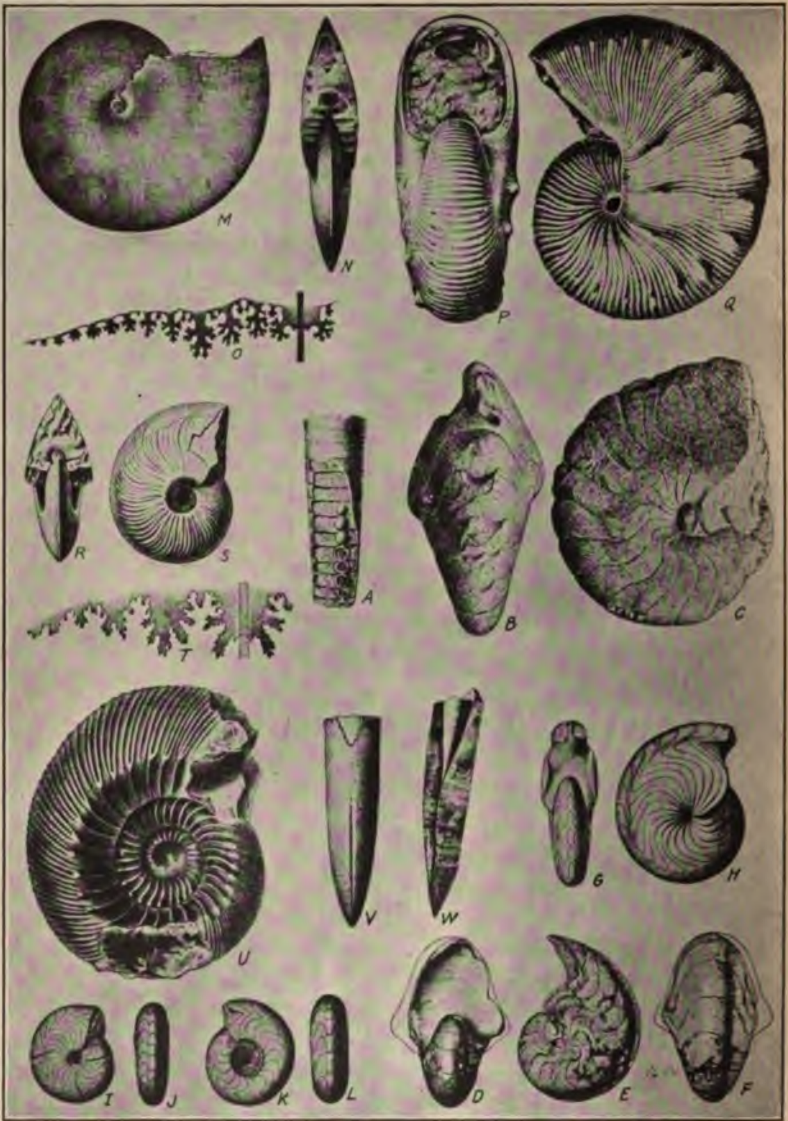

FIG. 37.—Fossil Cephalopod Shells. *A, Orthoceras* (*Loxoceras*) *monitiforme* (Hall), Ordovicic; *B, C, Nautilus* (*Hercoglossa*), *tuomei* Clark & Martin; Eocenic; *D, E, F, Nautilus* (*Hercoglossa*) *ulrichi* (White), Eocenic; *O, H, Goniatites* (*Aganides*) *rotatorius* de Kon. Mississippic; *I, J, Goniatites* (*Muensteroceras*) *parallelum* (Hall), Mississippic; *K, L, G.* (*Muensteroceras*) *oweni* (Hall), Mississippic; *M, N, O, Ammonites* (*Sphenodiscus*) *lenticularis* (Owen), with suture; Cretacic; *P, Q, Scaphites nodosus* var. *brevis* Meek, Cretacic; *R, S, T, Ammonites* (*Cardioceras*) *cordiformis* M. & H., with septum, Jurassic; *U, Ammonites* (*Olcostephanus*) *loganianus* Whiteaves, Comanchic; *V, W, Belemnites densus*, guard and section of same, showing inner shell or phragmacone, Jurassic. (All reduced.) (*After Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

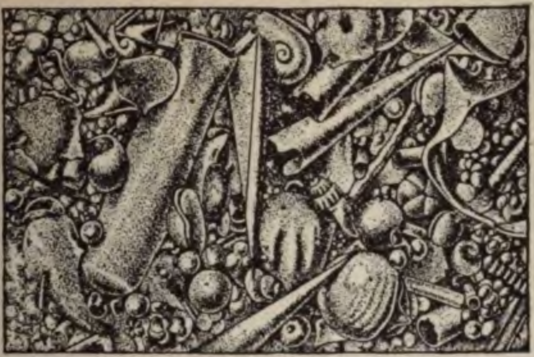

FIG. 38.—A mass of Pteropod shells from a deep sea pteropod ooze. Enlarged 10 diameters. (*After Murray and Renard.*)

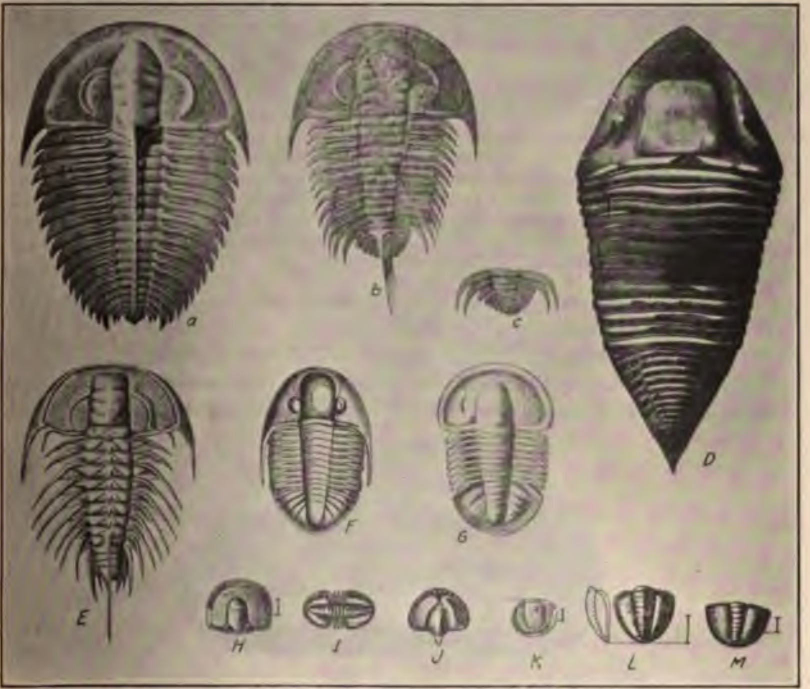

FIG. 39.—Types of Trilobites. *a*, *Holmia bröggeri* Walc., L.Cambric; *b*, *c*, *Mesonacis asaphoides* (*Emmons*) entire, and pygidium with last thoracic segments, L. Cambric; *D*, *Homalonotus delphinocephalus* (Green), Siluric; *E*, *Zacanthoides typicalis* Walc., M. Cambric; *F*, *Bathyurus extans* Hall, Ordovicic; *G*, *Asaphiscus wheeleri* Meek, M. Cambric; *H*, *K*, *Microdiscus acadicus* Hartt, M. Cambric; *I*, *Microdiscus speciosus* Ford; *L*, pygidium enlarged, L. Cambric; *J*, *M*, *Microdiscus pulchellus*, Hartt, M. Cambric. (*A-G*, reduced.) (*After Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

specimens. This leaf has a hollow, flattened mid-rib perhaps an inch in diameter, with nodes at intervals of a few inches, at which points the tube of the mid-rib is closed to form a series of floats. The growth is in the lower part of the leaf, which must not be cut.

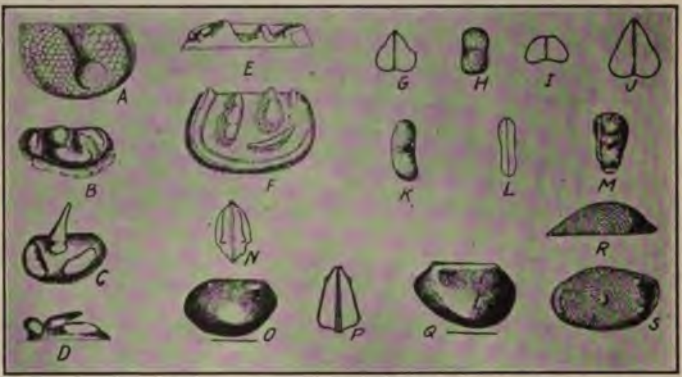

Fig. 40.—Various Types of Ostracoda. *A, Primitia seminulum* Jones, ×12, Devonic; *B, Hollina antispinosa* (Ulrich), ×7, Devonic; *C, D, Aechmina abnormis* (Ulrich), ×7, Siluric; *E, F, Drapanella crassinoda* (Ulrich), ×7, Ordovicic; *G, H, I, Metacypris consobrina*, Jones; dorsal, lateral (left) and posterior views ×13, Cretacic (fresh water); *J, M, subcordata*, Jones, dorsal view, ×13, Cretacic (fresh water); *K, L, Cytherideris impressa*, Jones, lateral and dorsal views, ×13, Cretacic (fresh water); *M, N, Cythere monticula*, Jones, lateral and dorsal views, ×13, Cretacic (fresh water); *O, P, Q, Leperditia angulifera*, Whitf. Siluric; *R, S, Primitiopsis punctulifera* (Hall), ×12, Devonic. (*From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

The species is perennial, and abounds in the tideways along the Alaskan Coast. For analysis of ash, see Table XX.

Nereocystis luetkeana (Fig. 51, p. 104).—This form has a length of stipe of 40 feet, but occurs both longer and shorter. It terminates on one end in a spherical float or pneumatocyst 7 or 8 inches in external diameter, and with a wall less than an inch in thickness. The lower end of the stipe ends in a "hold fast." From the float opposite the stipe spring several long, string-like leaves formed by division of an initial leaf.

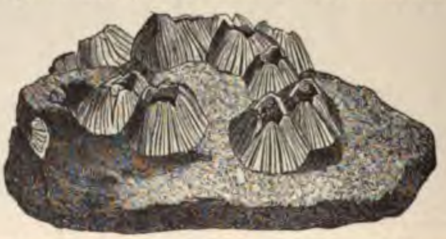

Fig. 41.—A group of barnacles attached to a stone. (*Balanus pictis.*) Miocenic. (*After Zittel.*)

This species grows in open water but is more commonly found in the tideways. It appears to be an annual, and propagates itself by means of spores which are formed in spots or *sori* on the leaves. For analysis of ash, see Table XX.

Pelagophycus porra.—This species probably contains more potash than the other three, but it occurs scattered on the seaward edge of the Macrocystis beds in quantities too small to be of importance.

Analyses of the ash of the three principal kelps dried in an oven at 105°C. gave the following results.

TABLE XX.—ANALYSES OF ASHES FROM KELP. ASH DRIED AT 105°C.[1]

	1 Macrocystis pyrifera	2 Alaria fistulosa	3 Nereocystis luetkeana
Average of number of analyses.....	58	15	51
Total soluble salts, per cent.........	30.0	24.4	46.9
Potash (K_2O).....................	12.59	9.1	20.1
Iodine (I)........................	1.57	Trace	0.13
Nitrogen (N).....................	....	2.6	1.9
Ash..............................	5.9	7.5	4.2
Range of Potash (K_2O), per cent.	....	2.9 to 13.1	6.58 to 31.62
Range of Nitrogen (N), per cent.	....	2.1 to 3.3	0.81 to 3.06

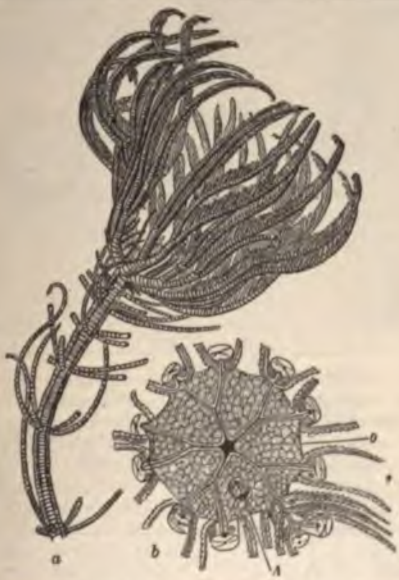

FIG. 42.—A modern crinoid *Pentacrinus caput-medusæ* Müller. *a.* Calyx with arms and part of stem. *b.* Oral surface enlarged showing central mouth (*o*) and eccentric anus (*A*). (*After J. Müller, from Felix Leitfossilien.*)

The production of potash (K_2O) from kelp in the United States in 1916 was 1,556 short tons, valued at the point of shipment at

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[1] For many detailed analyses see Burd, *loc. cit.*

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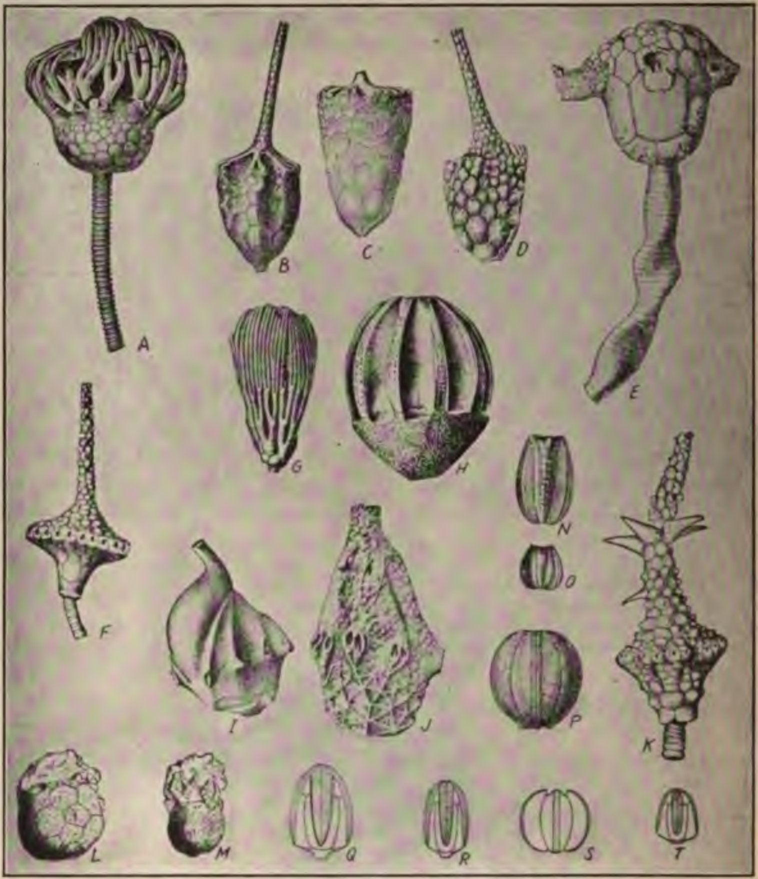

FIG. 43.—Fossil Crinoids. *A*, *Megistocrinus nobilis* W. & S. Mississippic; *B*, *D*, *Periechocrinus ornatus* Hall, Siluric; *C*, *P. tennesseensis* (Hall), Siluric; *E*, *Platycrinus halli* (Shumard), Mississippic; *F*, *Eutrochocrinus christyi* (Shumard), Mississippic; *G*, *Woodocrinus æqualis* (Hall), Mississippic; *H*, *Eucalyptocrinus elrodi* (S. A. Miller), Siluric; *I*, *J*, *Siphonocrinus nobilis* (Hall), internal mold, and exterior; Siluric; *K*, *Lobocrinus nashvillæ* (Troost), Mississippic; *L*, *M*, *Carabocrinus radiatus* (Billings), Ordovicic. Fossil Blastoids: *N*, *O*, *Elæacrinus elegans* (Conrad), *O*, ½ nat. size, *N*, part of one side, nat. size, Devonic; *P*, *Elæacrinus verneuili* var. *pomum* E. & C., × ½, Devonic; *Q*, *R*, *Pentremites elongatus* (Shumard), two varieties, Mississippic; *S*, *Granatocrinus norwoodi*, O. & S. Mississippic; *T*, *Pentremites conoideus* (Hall), Mississippic. (All reduced, *N* & *O* inverted.) (*From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

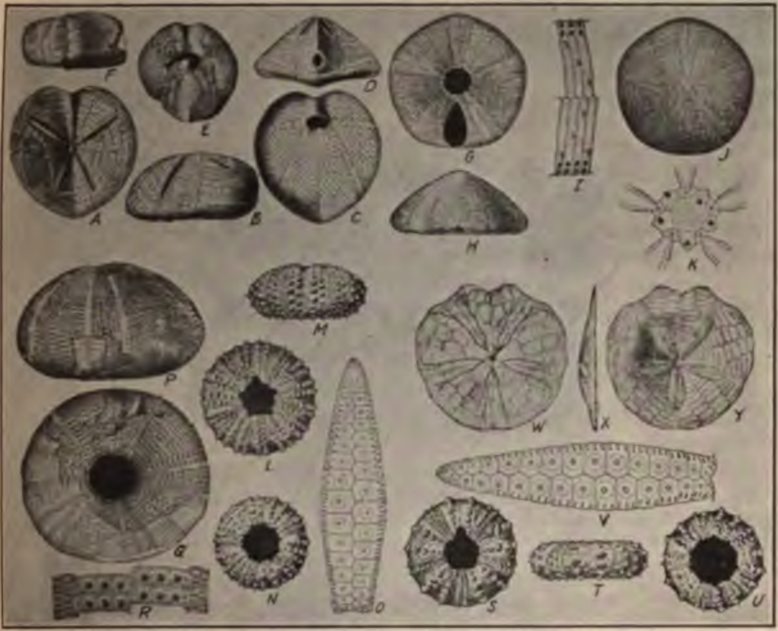

FIG 44.—Fossil Echinoids. *A to D, Linthia tumida*, Clark, Cretacic; *E, F, Echinocardium orthonotum*, Conrad, Miocenic; *G to K, Holectypus planatus*, Roemer, (*I*, shows ambulacral, *K*, apical systems enlarged), Comanchic; *L to O, Diplopodia texana* (Roemer); (*O* shows ambulacral area, enlarged), Comanchic; *P to R, Pedinopsis pondi* Clark, (*R* shows ambulacral plates, enlarged) Cretacic; *S to V, Diadema texanum* (Roemer), (*V* shows ambulacral area, enlarged), Comanchic; *W to Y, Scutella alberti* (Conrad), Miocenic. (All reduced, except where otherwise stated.) (*From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

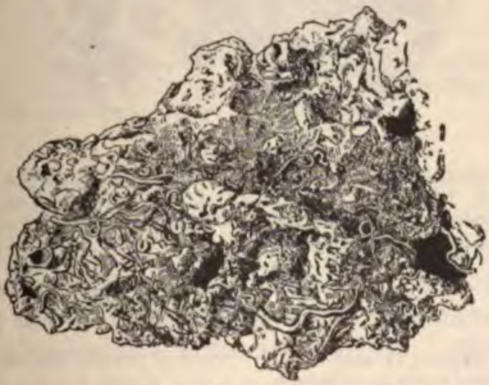

FIG. 45.—A mass of organic limestone consisting of corals, corallines, worm-tubes, echinoderm fragments, etc. Pourtales plateau, Atlantic ocean. (*After A. Agassiz.*)

depth below the surface. The species is probably perennial and has a life history certainly longer than a year.

Its distribution is reported from Sitka southward throughout the west coast of America. On the east coast it ranges from the southern end of South America to latitude 43° S. For analysis of its ash, see Table XX.

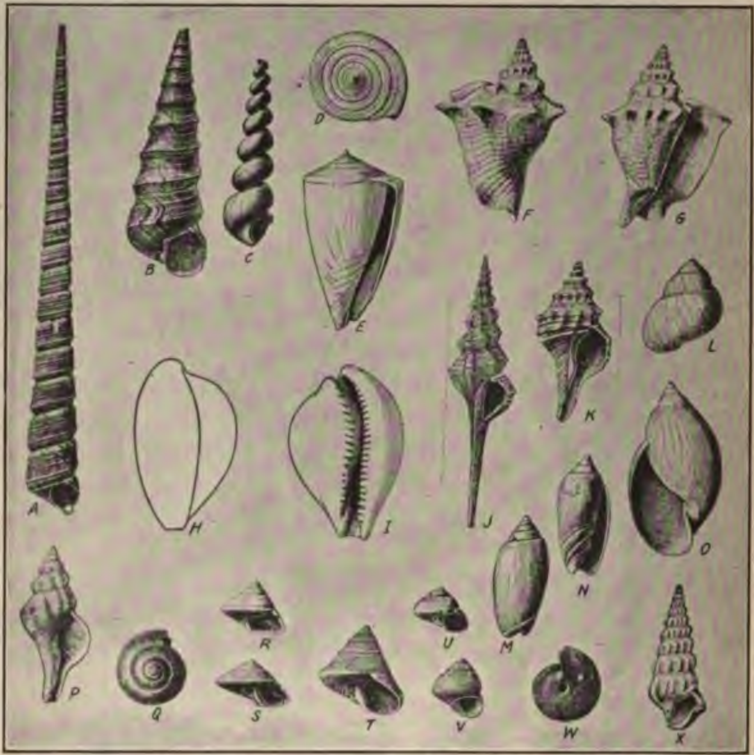

Fig. 34.—Types of Gastropod Shells. *A, Turritella cumberlandia* Conrad, Miocenic; *B, C, Turritella mortoni* Conrad, shell and internal mold, Eocenic; *D, E, Conus planiceps*, Dall, summit and side view, Oligocenic; *F, G, Strombus chipolanus*, Dall, Oligocenic; *H, I, Cypræa pinguis* Conrad, Eocenic–Miocenic; *J, Falsifusus meyeri* (Aldr.), Eocenic; K, *Urosalpinx strumosa* (Conrad), Miocenic; *L, Viviparus leai*, M & H, Cretácic; *M, N, Oliva literata* Lam. Miocenic-Recent; *O, Physa meigsii*, Dall, Pliocenic; *P, Lathyrus floridanus*, Heilpr., Eoc.-Mioc.; *Q, S, W, Calliostoma humele* (Conr.), Miocenic; *R, C. eboreum* (Wagner), Miocenic; *T, C. philanthropus* (Conr.) Miocenic; *U, C. aphelium*, Miocenic; *V, Gibbula glandula* (Conr.), Eocenic; *X, Potamides scalatus*, Heilpr., Pliocenic. (Mostly reduced.) (*From Grabau and Shimer, North American Index Fossils, A. G. Seiler & Co.*)

Alaria fistulosa (Fig. 50, p. 104).—This is a much smaller form with a stipe only about 8 inches long and ending in a "hold fast." From this arises a bunch of relatively small leaves, which are spore producers. From this bunch proceeds a long, rather fragile leaf, averaging 40 feet in length, and with an average width of less than 20 inches, but ranging up to 5 feet in some

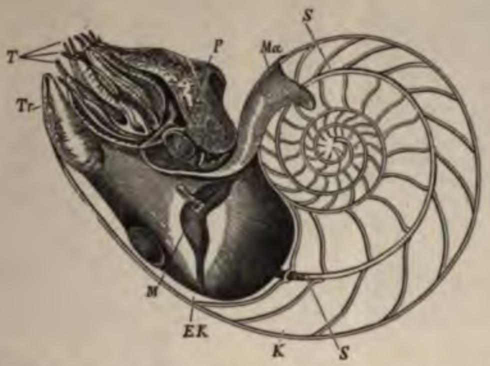

FIG. 35.—Nautilus. A living shelled cephalopod animal, with shell sectioned through median plane. *T.* Tentacles. *P.* Eye. *Ma.* Dorsal flaps of mantle. *Tr.* Funnel or hyponome. *M.* Adductor muscle. *S.* Siphon. *EK.* Living chamber. *K.* Air chambers. (*After Felix, Leitfossilien.*)

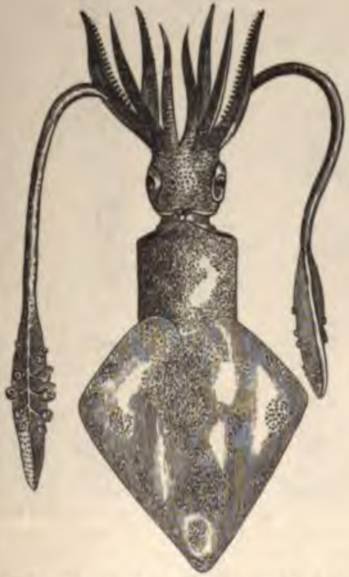

FIG. 36.—The modern squid (*Loligo vulgaris*). A living cephalopod with internal horny shell-remnant. Relative of the Belemnite. (*After Felix, Leitfossilien.*)

\$781,100.00.[1] In 1917 it was 11,306 tons containing 3,572 tons of pure potash (K_2O) valued at \$2,114,815. About one-fourth of the product consisted of dried and ground kelp, containing about 16 per cent. of K_2O. One-fourth was kelp charcoal and ash containing from 30 to 35 per cent. of potash (K_2O) and one-half was refined salt containing about 50 per cent. of K_2O.[2]

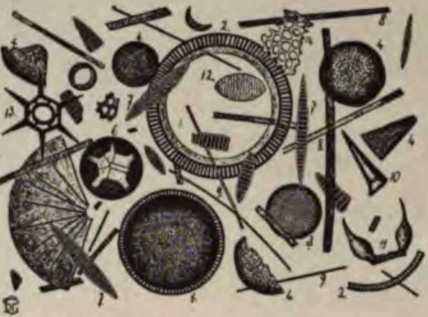

FIG. 46.—A group of diatoms from deep sea diatom ooze. Enlarged 200 times. 1–5. Coscinodiscus; 6. Asteromphalus; 7, *Fragilaria antarctica*; 8, 9. Synedra; 10. Rhizosolenia; 11. Chætoceras; 12. Navicula (?); 13, 14. Dictyochi and Radiolaria. (*After C. Chun, from Grabau, Principles of Stratigraphy.*)

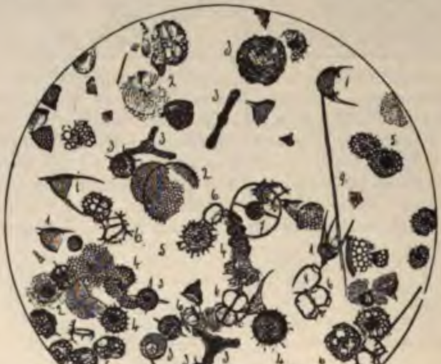

FIG. 47.—Radiolarian ooze from the Indian Ocean, enlarged 40 diameters. 1. Tricyrtida; 2. Dicyrtida; 3. Discoidea; 4. Prunoidea; 5. Larcoidea; 6. Coronida; 7. Sphæroida; 8. Chætoceras (Diatom); 9. Sponge spicules. (*After Krümmel from Grabau, Principles of Stratigraphy.*)

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[1] This is, of course, excessive. The price of potash has risen from 50 or 75 cents per unit to \$5.00 or \$6.00 per unit. A unit is 1 per cent. of potash per ton of material.

[2] H. S. Gale, Min. Res. for 1917, Pt. 4, p. 447.

The common sea-weeds of the Atlantic Coast (*Fucus*, *Ascophyllum*, *Laminaria*, Dulse, etc.) yield about 150 pounds of pure ash per ton of fresh plants, this containing over 9 per cent. or about 14 pounds of potash.

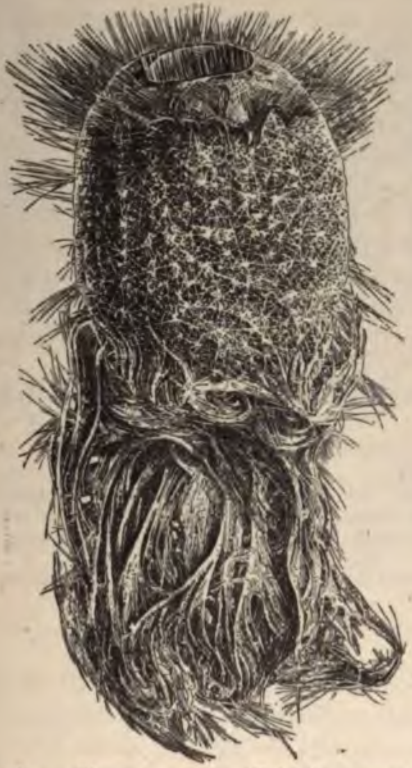

FIG. 48.—A modern siliceous sponge (*Holtenia carpenteri* Thoms.). This sponge has a skeleton of siliceous spicules and an anchoring basal device consisting of long glass fibers. (*After Felix, Leitfossilien.*)

Soda-Producing Plants[1]

On the Spanish Coast large quantities of soda were formerly obtained from a shore plant *Salsola kali L.*, belonging to the order Chenopodiaceæ. This was grown on large areas reclaimed from the sea by dams, and reduced to ash by ignition. The sinter ash thus obtained was called *barilla*, a name still used in

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[1] Von Buschmann, Das Salz, Vol. I, p. 527. Only coastal plants will be noted here, for others see Chapter XI.

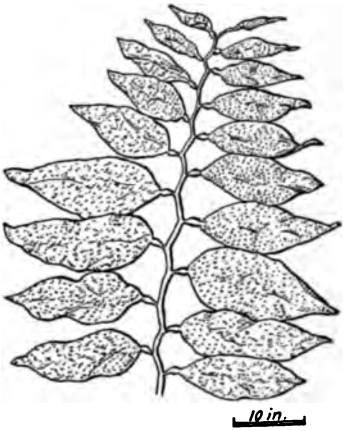

FIG. 49.

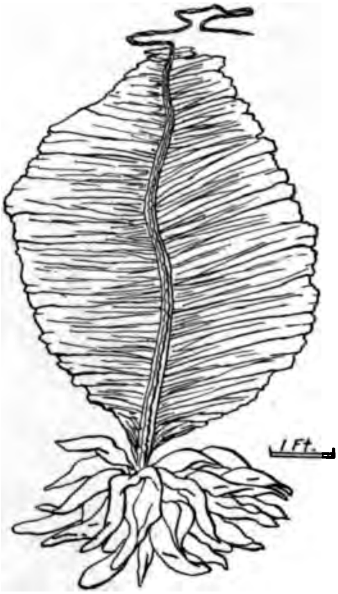

FIG. 50.

FIG. 49.—*Macrocystis pyrifera.* A modern, potash-secreting kelp from the Pacific Coast. (*From a Drawing by Mary Welleck.*)

FIG. 50.—*Alaria fistulosa.* A modern, potash-secreting kelp from the Pacific coast. (*Drawn by Mary Welleck.*)

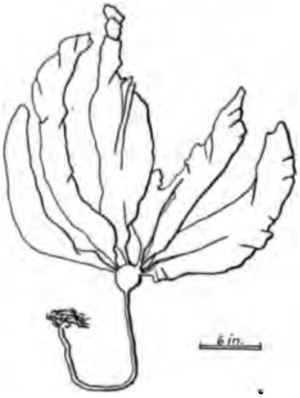

FIG. 51.—*Nereocystis luetkeana.* A modern, potash-secreting kelp from the Pacific coast. (*Drawn by Mary Welleck.*)

the trade. The barilla of Alicante on the Mediterranean Coast (S. E. Spain) was especially valued, carrying from 14 to 20 per cent. of carbonate of soda. This industry was brought to Spain by the Saracens, who called this plant *al kali* (*al* being the Arabian article). From this is derived the name alkali. 350,000 pounds of the barilla was still exported annually from Spain to England at the beginning of the 19th century. On the island of Lanzarote, the easternmost of the Canary Islands, barilla was formerly made from the "ice plant" *Mesembryanthemum crystallium*, which grows upon the coast, this industry forming the chief source of income of the inhabitants.

In this connection the soda-secreting plants of Armenia, cited in the discussion of the soda lakes of that region (p. 248) are of interest, as are also the potash salts of the Nebraska lakes, derived from land plants of that locality (see p. 257), and the plants which secrete salt ($NaCl$) in various countries.

B. CHEMICAL PRECIPITATION OF SALTS IN THE SEA

Under the term Precipitation Sea Salts, or marine precipitates, we designate those salt masses which have been precipitated from sea water by a chemical reaction with foreign substances introduced, instead of by the physiological activities of organisms or the direct deposition by concentration or from super-saturation.

Lime Salts

As in the case of the organic salts, carbonate of lime is the most important precipitation salt deposited in the sea. This is brought about by the reaction of the calcium sulphates and chlorides of the sea water with ammonium carbonate, which is the product of putrifying organic matter on the sea bottom. The reactions may be written as follows:

$$CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4.$$
$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

According to Linck, the carbonate of lime resulting by the reaction of the sulphate of lime with the carbonate of ammonia, is always aragonite and of spherulitic form. Calcite is, however, precipitated by this reagent and by sodium carbonate from solutions of calcium sulphate, otherwise free from salts, at temperatures of both 40°C. and 18°C.

Experiments made by Irvine and Woodhead[1] show that effete substances derived from living animals in sea water will bring about these results. They placed four small crabs, weighing 90.72 grams, in sea water absolutely free from carbonate of lime. After twelve months they produced an alkalinity in the water equal to the production of 45.36 grains of calcium carbonate. This was due to the decomposition of calcium sulphate by the uric acid and other effete matter.

In another experiment, 9 small crabs were allowed to die and to undergo complete putrifaction in 2 liters of sea water, at temperatures varying from 70° to 80°F. The result was the precipitation of all the lime salts in the form of carbonates.

After the removal of the calcium salts by precipitation, the magnesium salts will be precipitated, also in the form of carbonates. This has been shown by an experiment made by Murray and Irvine,[2] in which they added a quantity of urine to sea water, which on decomposing furnished alkaline carbonate. After a few days the precipitate given under *A* in the subjoined table was found. Filtering this out, and allowing the mixture to stand 10 days longer, the precipitate given under *B* was obtained. These precipitates gave on analysis the following composition.

TABLE XXI.—ANALYSES OF PRECIPITATES BY URINE FROM SEA WATER

	A	*B*
Water and organic matter (containing 7.38 per cent. ammonia in *A*)	21.81	20.25
Carbonate of lime	4.85	75.35
Phosphate of magnesia and ammonia	51.10	
Phosphate of lime	12.24	
Carbonate of magnesia	.....	1.02
Phosphate of magnesia	.....	3.38
	100.00	100.00

The carbonate of magnesia was precipitated after much, and perhaps nearly all of the calcium was precipitated, chiefly as carbonate. This would indicate that dolomites are deposited only in waters from which much of the lime has previously been removed, either by lime-secreting organisms or by chemical precipitation.

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[1] Proc. Roy. Soc. Edinburgh, Vol. XV, pp. 308–316; Vol. XVI, pp. 324–354; Vol. XVII, pp. 79–108.

[2] Proc. Roy. Soc. Edinburgh, Vol. XVII, pp. 79–109 (104).

That such deposition of lime is not more common in the open ocean, is due to the fact that decaying organic matter is rare on the sea floor, for it serves as food for the countless scavengers which inhabit the sea. Only in nearly enclosed basins, such as that of the Black Sea, where vertical circulation is slight, and where scavengers are few or absent, can deposits of this type go forward. Here only anaërobic bacteria, especially *Bacterium hydrosulphuricum ponticum* can live, and these separate H_2S from the sea water, which combines with the iron in the sediment and results in the abundant formation of iron sulphide and free sulphur. The abundant development of ammonium carbonate in the lower layers of the water of the Black Sea, due to the decomposition of the dead organic matter on its bottom, causes the formation of a powdery precipitate of $CaCO_3$ which, at a distance from the shore, where mechanical detritus is less abundant, forms layers and thin banks of fine-grained limestone.[1]

Calcium and magnesium carbonate appear also to be depositing under the influence of decaying organic matter on the bottom of the Bay of Naples. Here Walther and Shirlitz[2] found a fine, calcareous and magnesian mud, which seems to have been separated by chemical reaction from the lower strata of the water of the bay, these strata being poorer in lime and magnesia than the upper. The mud is relatively poor in organic remains.

Manganese and Other Salts

Next to the precipitation of lime salts by chemical reaction, the formation of manganese salts takes rank. This salt is precipitated chiefly in the form of the oxide associated with iron oxide, and with clay and silica to form concretions which are widespread over the deeper parts of the ocean floor. These concretions generally form about foreign bodies, such as pieces of pumice or the earbones of whales, etc., and their restriction to the deep sea shows that their formation is a slow one.

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[1] See further, The Black Sea basin, Vol. II.

[2] J. Walther and R. Shirlitz, Studien zur Geologie des Golfes von Neapel. Zeitsch. d. deut. geol. Gesellschaft Bd. 38, p. 306, 1886.

The quantity of manganese in normal sea water is a very small one, occurring in the form of the bicarbonate. It has been held that on coming in contact with the oxygen of the air, the peroxide of manganese is formed. On the other hand, the origin of these deposits has been referred to the decomposition of basic volcanic rocks in the sea, they being thus a diagenetic product (meta salt). Submarine volcanic eruptions and springs have also been held responsible for the formation of these concretions. The entire subject has been summarized by Potonie[1] and to this paper the student is referred for further details.

C. DEPOSITION OF SEA SALTS FROM SUPERSATURATED SOLUTIONS, AND BY CONCENTRATION

The saline constituents of sea water, as of all waters, will in general be deposited in the reverse order of their solubility upon the concentration of the solution, as already outlined in the preceding chapter. The solubility of a simple salt in pure water is, however, a different thing from the solubility of that salt in the presence of other salts, for the solubility of each one of the salts is affected by its associates in the solution, the whole having rather the character of solutions within solutions. Moreover, temperature is an important determining factor, as has been shown abundantly by the researches of Van't Hoff and his associates. Again, the influence of time must be taken into consideration, for it is a very important factor in the formation of the more complex salts.

Supersaturation

It may be well to consider separately the supersaturation of normal sea water with a given substance, owing to the abundant local supply of that substance, without the accompanying concentration of the sea water. Of all the salts of the sea water, calcium carbonate most commonly falls under this category.

According to the experiments of G. Linck[2] the maximum solubility of calcium carbonate in sea water at 17° to 18°C. is about 0.191 grams of CaCO, per liter, or 0.0191 per cent. while the experiments of Cohen and Raken[3] indicate that the maximum is

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[1] Naturwissenschaftliche Wochenschrift, Bd. V.

[2] Neues Jahrbuch für Mineralogie, etc., Beilage, Bd. XVI, p. 506.

[3] Proc. Sec. Sci. Amsterdam Acad., Vol. 3 , 1901, p. 63.

0.1264 grams per liter. As the total amount of $CaCO_3$ in sea water according to the determination of Ditmar (p. 51) is only 0.121 grams per liter it is apparent that normal sea water is undersaturated for this salt.

If the maximum is exceeded, deposition of the lime will occur, which will be in the form of calcite in temperate climates, and in that of aragonite in tropical climates. According to Irvine and Young,[1] amorphous calcium carbonate, such as is secreted by marine lime-secreting organisms, is more soluble in sea water than the crystalline salt, only 1,600 parts of sea water being required to dissolve one part of amorphous $CaCO_3$, whereas 8,000 parts of sea water are needed for one part of crystalline lime. This indicates that supersaturation is most readily produced in the vicinity of coral reefs, and other lime deposits of organic origin.

Supersaturation may occur in the neighborhood of limestone coasts in tropical waters, or where streams bring in an abundance of calcium carbonate in solution. Thus in the neighborhood of coral reefs, where the amount of lime appears to be large in spite of the fact that organisms constantly remove it, secondary deposition of lime goes on in the cavities and in spaces between the coral and other organic lime masses, as well as in the clastic lime sand which results from the destruction of the reefs by waves and otherwise. In consequence, the reef materials, as well as the lime sands around coral reefs, are cemented into a solid mass. On shores rich in lime, particles of foreign matter, such as broken shells, grains of igneous rock, fragments of quartz, and even the eggs of insects, are encrusted with lime carbonate, forming oöloidal deposits, though these can not be regarded as true oolites. Examples are known from many tropical coasts, such as that of Ascension Island, Tahiti, the Gulf of Mexico, and elsewhere. In partly enclosed bodies of sea water such as the head of the Red Sea and the coast of the Sinai Peninsula, true oölites seem to be formed by such precipitation of lime. This, according to Linck, is in the form of aragonite. On the coast of Gran Canaria in the Canary Islands, such lime-encrusted foreign particles are further cemented by lime into a solid rock, which is quarried at low tide. The water here has a temperature of 20°C., or over, throughout most of the year, and appears to be abundantly charged with $CaCO_3$ probably derived from local solution of lime rocks which it redeposits in favorable sections to form a recent limestone.

[1] Proc. Roy. Soc. Edinburgh, Vol. 15, p. 316, 1888.

On the north coast of Brazil, a remarkable series of stone reefs is formed by the precipitation of calcium carbonate in the shallow sea water. These are of the nature of bars which extend across the mouths of streams some distance from shore though one end of the bar is generally connected with the shore, at least at low tide.[1] These reefs extend in a more or less interrupted line for 1,250 miles along the northeastern part of the Brazilian coast, from Ceará to Porto Seguro, between south latitudes 3 degrees 43 minutes, and 16 degrees 30 minutes. The best known example is at the Port of Pernambuco, where it was noted by Darwin. Where exposed above the water, "the reef rock is sandstone, often almost as hard as a quartzite, and ringing under the hammer like a clinkstone, but sometimes and locally it is only moderately hard. It contains abundant shells and other remains of animals and calcareous plants, apparently of the same species as those now living in the ocean alongside. The beach sands in the vicinity of the stone reefs invariably contain similar remains and abundant small fragments of shells, corals, and of other lime-secreting organisms. Except in the matter of hardness and compactness, the rock of the reef is therefore scarcely distinguishable from the present beaches. The cementing material of the hard rock is lime carbonate, which sometimes contains a little iron also. The rock has a remarkably fresh appearance, and the shells embedded in it usually retain their bright colors."[2]

The strata dip oceanward at an angle of from 2 to 20 degrees the smaller angle prevailing. The thickness of the hard rock as shown by borings ranged from 2.95 to 4 meters, and it rests on loose sand and shell material or on clay. The width of the stone reef, which is flush with the surface of the water at high tide, varies from a few paces to 450 feet, and the length from a few hundred feet to 8½ miles.

Branner concludes from extensive study of these reefs that the consolidation is due to the precipitation in the sea water of the excess of lime brought by streams from fresh pools along the shores, where abundant aquatic and semi-aquatic plant life furnishes acids by their decay which enable these streams in percolating at low tide through the embankments of calcareous sands to dissolve their lime, which then separates out on coming in contact with the sea water here rendered denser than normal under the tropical conditions. Similar stone reefs exist on the coast of Asia Minor in the Mediterranean.[1]

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[1] J. C. Branner, Stone Reefs on the Northeast Coast of Brazil. Bull. Geol. Soc. America, Vol. XVI, pp. 1–12, pls. 1–11, 1916.

[2] Branner, *Loc. cit.*, p. 2.

Concentration

Concentration of sea water is brought about by evaporation, and it is therefore apparent that in the open sea no concentration products can be formed, since the free circulation of ocean waters immediately makes good the loss by evaporation. This will be apparent when it is remembered that sodium chloride is deposited only when the normal sea water has been evaporated to about one-tenth its original bulk. Thus, taking the mean depth of the ocean as 3,680 meters, the surface would have to be lowered more than 3,000 meters by evaporation before salt deposition would begin on the floor of the ocean. No deposition of salts of any kind occurs until the volume has been concentrated to nearly one-half its original bulk (see *ante*, p. 54).

Concentration products are of two kinds—the simple salts deposited directly from the water when proper concentration is reached, and the double salts, which result from combination of two or more salts as previously discussed. The double salts formed from sea water are mostly deposits from the mother liquor, though some of them may be derived subsequently by reactions among simple salts (diagenetic processes).

Conditions of Deposition of Concentration Salts From the Sea

Since concentration of sea water is brought about only by evaporation, and since evaporation of the water of the open ocean is compensated for by the ocean currents, it is evident that before concentration can take place a certain amount of isolation of the water to be concentrated is necessary. This is effected in coastal lagoons and salt pans in cut-off portions of the sea and indirectly by the inclosure of salt water in the sediments. No amount of isolation, however, is effective unless evaporation is in excess of the amount of water supplied by precipitation, by affluents or by springs. It is evident, therefore, that climate is a very important factor, and this may be briefly considered.

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[1] For details regarding the causes responsible for the localization of these stone reefs the student should consult Branner's paper.

The Climatic Factor.—The one universal factor active in the production of salt deposits is the climatic one. In all cases where salt is to be abstracted from a body of saline waters by concentration, evaporation must exceed precipitation. Comparative aridity of climate is the most important condition requisite for the formation of salt at the present time, and conversely the occurrence of salt deposits in the earth's crust unequivocally points to the existence of arid conditions at the time of the deposition of the salt. Extreme aridity is not necessary, all that is required is that the annual precipitation should fall sufficiently below the abstraction by evaporation.

The conditions most favorable for the production of arid climates are those which involve drying winds. These are found primarily on the leeward side of comparatively high mountain chains, which extend across the path of prevailing winds, and intercept the moisture-bearing air currents, and, by forcing them to rise in order to cross the obstruction, also force them to part with a large portion of their burden of moisture. The windward sides of such mountain chains are thus abundantly watered, and as a consequence they are clothed with vegetation. The leeward side, on the other hand, where these winds in descending become warm, drying winds, is correspondingly arid, and supports little, if any, vegetation. These features are especially marked in the pathways of the constant or planetary winds, such as the easterlies or trade winds, which blow in the zone between the equator and 30°N and S latitude, and the westerlies which blow in the opposite direction in the belt bounded by the 30° and 60° parallels, both north and south latitude. Where seasonal winds or monsoons overcome the planetary winds, a reversal of moist and dry climates may occur.[1]

It is apparent that water bodies which lie in the lee of the mountain barriers are subject to evaporation under the influence of the drying winds. The open sea, of course, will not be affected in any appreciable degree by these conditions, though the coastal strip between the mountains and the sea may be in large part a desert. This is the case with the western slope of the Andes Mountains, which intercept the southern trades. The Atacama and other deserts which occupy a large part of the belt between the Andes and the Pacific Coast in Peru are among the driest and most barren deserts of the globe. The following diagram

[1] See further, A. W. Grabau, "Principles of Stratigraphy," pp. 40–50.

illustrates the conditions of the formation of deserts in the lee of mountain chains which intercept the planetary winds (Fig. 52).

Absolute and Relative Humidity of the Air.—The absolute humidity of the air is the total amount of water which it contains. This may be measured by noting the vapor pressure. At Batavia on the Island of Java where the mean annual temperature is 25° to 26°C. and where the moisture-bearing monsoons from the Indian Ocean are the dominant factor in the climate, the vapor pressure is about 21 millimeters, corresponding to an amount of water vapor in the air of 2.8 per cent. by volume. Here the composition of the atmosphere is nitrogen, 76.8 per cent.; oxygen, 20.4 per cent.; water, 2.8 per cent. and a few hundredths of 1 per cent. of carbon dioxide. At Allahabad on the Ganges in India,[1] the vapor pressure observed once during the rainy season was 30.7 mm., corresponding to 4 per cent. by volume of water vapor. In central Europe, even in summer, the vapor pressure is around 10 mm., the amount of water vapor being only 1.3 per cent. The amount of water vapor which the air can hold, or its saturation, varies of course with the temperature. Expressed in weight of water, the amount which one cubic foot of air can hold is as follows: at 0°F., ½ grain; at 60°F., 5 grains; at 80°F., 11 grains; at 60°F. the air of a room 40 × 40 × 15 feet can hold nearly 20 pounds of water or almost enough to fill a common water pail. At 80° it can hold more than twice that. The air, however, is saturated only at the point when precipitation is about to take place (dew point). Ordinarily the amount of water vapor in the air is less than that which it could contain at that temperature and in dry climates (as distinct from hot climates) it is very much less. The percentage of water vapor

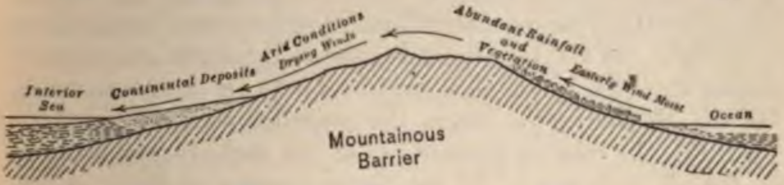

FIG. 52.—Diagram illustrating the development of arid conditions on the lee side of a mountain chain, with the corresponding formation of continental deposits and marine salts on the borders of an interior sea. (*From Principles of Stratigraphy.*)

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[1] Hann, "Handbook of Climatology," Transl. by Ward, p. 74.

which the air contains of the amount which it could actually hold at that temperature, is called its *relative humidity*. Thus if the air contains only half the amount of water vapor which it could contain at that temperature, its relative humidity is 50 per cent. If it is saturated its relative humidity is 100 per cent.

The average relative humidity of the air over the land, is perhaps 60 per cent. while over the oceans it is about 85 per cent. Where the average relative humidity falls below 65 per cent. the air is said to be dry. In semi-arid regions the relative humidity ranges around 45 per cent. and in desert regions around 25 or 30 per cent. This, it must be borne in mind has no direct bearing on the temperature of the region, for there are cold dry and hot moist regions. In the latter the absolute amount of water vapor in the air is, of course, very great. Thus at Batavia on the island of Java about 6° south of the equator the relative humidity is 83.3 per cent. (1891) with a mean annual temperature of 25.78°C. (78.4°F.), while at Dorpat in the Baltic Provinces of Russia about 58° north of the equator it is 73 per cent. in summer. On the Mediterranean where the mean temperature is 16.6°C. (61.9°F.), the relative humidity is 69 per cent. (vapor pressure of the air 10.5 mm.). In the desert country of North Africa the relative humidity is very low. Thus at Ghadames, western Tripoli, it is 27 per cent. in July and 33 per cent. for August. The oasis of Kufra in the heart of the Libyan desert has a relative humidity of 27 per cent. for August as a whole, but only 17 per cent. for the 3 P.M. August mean. For September the mean relative humidity is 33 per cent. The oasis of Kauar (or Kawar) in the Sahara, has a mean relative humidity of 27 per cent. in August. In the Punjab district of India at Lahore, northern part of Indo Gangetic plain, Indus drainage, the relative humidity for May is 31 per cent., while at Agra (North West province) on the Jumna (south side of the Indo-Gangetic plains, Ganges drainage) it is 36 per cent. In the Death Valley, California, the mean relative humidity for the five months from May to September, 1891 was 23 per cent.

Evaporation.—This is of course greater where the relative humidity is low. Where however the temperature is also low, and therefore the total amount of water which the air can contain is small, saturation is soon reached unless the dry air is constantly replaced. Where the temperature is high, evaporation may be much greater even in stagnant air, but where this air is in motion it will be very rapid and extreme. Hence the importance of drying winds, *i.e.*, winds of low relative humidity.

The evaporation of the water from the surface of the Mediterranean and Black Seas is estimated at more than 226 cubic miles per annum. It is estimated that the average amount of the evaporation from the surface of the earth each year amounts to a layer of water 30 or 40 inches deep.[1] At this rate, if the water were not returned to the sea, the oceans would become dry in 3,000 to 4,000 years, while the lakes of the earth's surface would probably all disappear in a single year. It is thus understood how the water of playa lakes which is seldom more than a few feet in depth and may be many hundreds of square miles in extent, may evaporate in a few days.

The Isolation Factor.—No amount of aridity will, however, result in the formation of salt deposits unless isolation of portions of the sea water is effected. Such isolation can only be brought about by the formation of barriers which, for a time, at least, keep out the sea water from the area separated and thus permit the evaporation of the isolated portion of the sea. Such barriers are of various kinds and they and the deposits found behind them will be discussed in the next chapter.

In the manufacture of common salt in sea salinas, this isolation is brought about by shutting off the inlet when the salt pans are flooded to a given extent and only opening them again when the crop of salt is harvested, or in the case of more complex salinas, when the brine, concentrated in the evaporation basins is transferred to the crystallization basin where the salt separates out. (See further descriptions of sea salinas in Volume II.)

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[1] Some estimates make it as high as 60 inches.

CHAPTER V

SEA MARGIN DEPOSITS OF SALT

The evaporation of sea water along the coast may under proper conditions of isolation give rise to extensive deposits of sea salts. Such deposits may be classed under the following three groups: (*a*) Marginal salt pans, (*b*) Marine salinas, and (*c*) Lagoonal deposits. All of these have certain common characteristics, most notable among which is the fact that the ocean or other marine body furnishes a constant source of supply from which the salts are progressively abstracted by condensation to the point of oversaturation or by complete evaporation at intermittent periods.

A. MARGINAL SALT PANS

These are shallow depressions along the sea margin, often of great areal extent, into which the sea water is poured at high tide or during storms, or they are broad expansions of flat country over which a shallow film of sea water is spread during periods of exceptional high water, and from which it evaporates before it is able to recede again. Artificial salt pans have been constructed along many coasts where climatic conditions favor evaporation, and these often serve as an important source of salt supply. Into these the sea water is commonly led by specially constructed canals. (See Vol. II.) A few of the more characteristic natural salt pans will be considered.

The Rann of Cutch.—This, the most famous of the natural salt pans, lies on the western coast of India, in the Bombay Presidency and south of the mouth of the Indus. The Gulf of Cutch separates the peninsula of Kathiawar on the south from the Island mass of Cutch on the north. Continuing inland from the gulf is the Rann, and this connects northward with the Great Western Rann, which completely surrounds the Cutch land mass on the north. The Rann is a low, flat plain of sandy clay, plentifully impregnated with salt, which keeps its surface always moist. Scattered over its surface are shallow pools of salt water. Its extent is about 300 kilometers in length, by almost 100 kilometers in greatest width. Its area is about 18,000 square kilometers (7,000 sq. miles) and it probably has not its equal anywhere on earth. It merges laterally into the *Put*, which consists of planes free from vegetation and which in turn is surrounded by the sand dune region, the so-called *Thurr*. This is characterized by dunes from 25 to 130 meters in height, separated by flat areas on which are found lakes which range in depth up to 20 meters. The Thurr is inhabited by foxes, jackals, wolves, rats, snakes, etc., while the area of the Rann is practically free from animal or vegetal life, and there is in all this region not a drop of fresh water. It is a veritable "*terra hospitibus ferox*" (see Fig. 53).

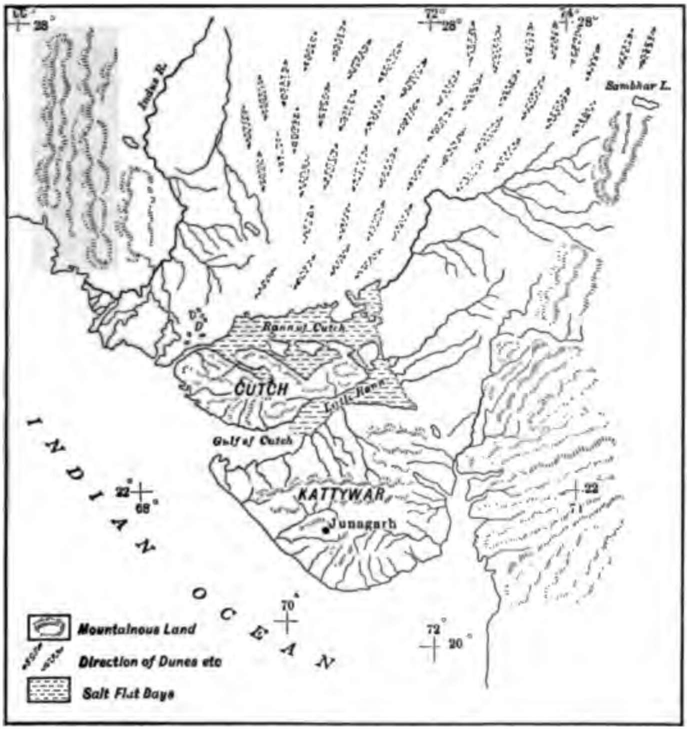

Fig. 53.—Outline map of a part of northwest India, showing the location of the Rann of Cutch, the Kathiawar (or Kattywar) Peninsula, Sambhar Lake and other districts mentioned in the text.

During the summer months the southwest monsoon winds sweep in from the Arabian Sea, and entirely displace the northeast trade winds normal for this region. As a result, the water rises over the Rann, more or less completely flooding it, in some places to the depth of a meter. In winter when the northeast monsoons blow in harmony with the northeast trades across the Himalayas, arid conditions are developed and the salt water which has been retained in the pools becomes subject to evaporation, and they are covered with crusts of pure salt, which, however, is generally only about 10 cm. in thickness but may occasionally reach the depth of a meter or more. The plain itself is often encrusted by a layer of salt up to an inch (2½ cm.) in thickness, or covered with beautiful salt crystals.

It is, of course, evident that no extensive salt deposits can form in this region, for the semi-annual flooding of the plain by sea water only a little above the normal in salinity will redissolve the salts which have formed during the dry winter season in so far as they have not been removed by man. Much of the salt of the Bombay Presidency is, however, produced along the coast by solar evaporation of sea water (see Vol. II).

The Salt Pans of the Red Sea Coast of Erithræa.—West of Amfila Bay on the Erithræan Coast of the Red Sea (East Africa), is a remarkable salt pan, the floor of which lies below sea level. It is surrounded by a wall of gypsum and besides being periodically flooded by the waters of the Red Sea, it receives the intermittent drainage from the Abyssinian Mountains, which is highly charged with saline ingredients. By the evaporation of the water in this pan, salt deposits are formed, with which are regularly associated deposits of gypsum. To what extent mother liquor salts are formed here is not known. Probably all of the mother liquor is removed again on the incoming of the next flood.

Farther south lies the salt pan of *Allolebod*, which is of considerable extent. Here the salt is regularly interstratified with layers of gypsum, which represent the first precipitation after each inundation from the Red Sea. These layers protect the salt beds below them, and thus a regular stratified series, comparable to some older rock salt deposits, is built up. The depth of the deposit is not known, but from the nature of the case cannot be very great.

Natural salt pans abound on the east coast of the Sinai Peninsula (Gulf of Akabah) and at one time furnished all the salt of that peninsula.[1]

[1] Von Buschmann, Das Salz, Vol. II, 201.

The conditions favoring the development of these salt pans is somewhat peculiar. They lie within the belt of northeast trades which sweep across the Red Sea and therefore are moisture laden. These winds impinge against the mountain ranges which form the Abyssinian (Erythræan) and Egyptian coasts of the Red Sea, and are precipitating rather than drying winds. The winter monsoons, however, blowing outward from the region of high pressure in the Great deserts of North Africa, toward the Indian Ocean, which is then a region of low pressure, become the chief factor in the production of semi-aridity along the western coast of the Red Sea, whereas the flooding of the natural pans takes place during the summer months when the monsoons are in harmony with the trades.

Salt Pans of the Nile Delta.—Numerous natural salt pans are scattered along the coast of the Nile Delta between Alexandria and Port Said. They are periodically flooded by waters from the Mediterranean, which then evaporates under the influence of the semi-arid climate. The salt thus produced is often covered by wandering sand dunes which by their heat dry up the mother liquor, its salts becoming dispersed by the wind. The dune sands often contain crystals of gypsum 3 to 5 cm. long, which may unite into heads up to a meter in thickness and with a diameter of 4 meters (Fig. 54).

In the salt pan of Mex near Alexandria on the Nile delta, a salt bed from 7 to 14 cm. in thickness is formed every year. Walther remarks, that if the floor of the basin were to subside that amount annually, a salt bed of the thickness of the Stassfurt deposit would form here in 3,500 years, while throughout this time there would be an average depth of water in the basin of only about 50 cm. The salt here is well bedded, of a coarsely crystalline texture consisting of large intergrown crystals. It rests upon a black slime permeated with decaying organic material.

The annually formed salt-cover of this pan is solid as an ice sheet, but ripple marks 5 cm. wide and 1 cm. in height are found upon it. These are formed by solution caused by the rain water in spring, which then forms a shallow layer over the salt, partly dissolving it, and which is rippled by the wind. The surface of the plain when dry becomes divided into polygonal fields separated by ridges of salt varying from 5 mm. to 3 cm. in height, according to the size of the polygons.

Walther found few living organisms in the salt water of the

Mex salt pan. *Artemia* (Fig. 82, p. 241) a small salt water crustacean, formed small red spots in the water, and another small red crustacean about 4 mm. long, was crawling on the bottom. *Artemia* was found by Walther in such abundance in the salt pans near Suez that the water looked like diluted blood, while beneath a bed of white salt 5 mm. in thickness, he found a salt bed colored red by the abundant enclosure of this crustacean. Below this, in turn, he found a yellow clay 2 cm. in thickness, and beneath that a shell breccia which has a wide distribution along the Gulf of Suez.[1]

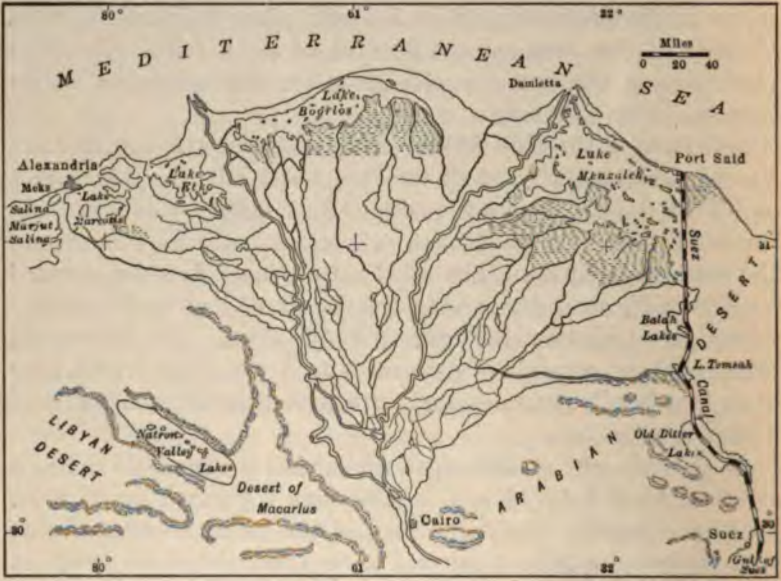

FIG. 54.—Outline map of the Nile Delta, showing the distributaries, the salt lagoons and marshes, the location of Natron Valley and the Bitter Lake of Suez.

Salt Pans of the Black Sea Coast.—The northwest coast of the Black Sea (Bessarabia and Khersan) is characterized by numerous sea salt pans, which lie mostly on the flat delta plains of the rivers, especially the Danube and the Dnieper, as well as the rivers lying between them. Many of the rivers become enlarged at their mouths into lagoon-like water bodies which are separated from the sea by a sand bar thrown up by the waves.

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[1] J. Walther, Gesetz der Wüstenbildung, 2d Ed., pp. 241–243.

These water bodies are known as *limans* and many of them are filled with salt water, which enters the liman through the narrow passage in the bar. In summer, when the streams dry up, many of the limans will also become dry, leaving a deposit of salt behind. This is especially the case with the limans of the Bessarabian Coast. In the Dudle liman, the salt crust is often a foot in thickness near the center and is extensively worked during the summer months. The salt crust rests upon a thick bed of tenaceous, slimy sediment brought by the streams during the rainy season. In this the salt workers are sometimes mired, and the fatalities are at times considerable (Fig. 55).

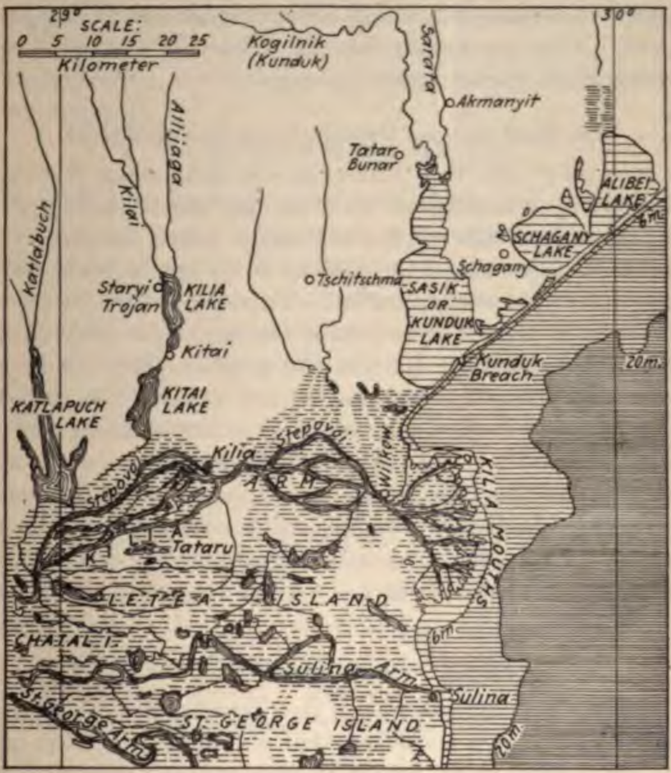

FIG. 55.—Map of the marginal lakes or *limans* of the Black Sea coast (Bessarabia) and of the Kilia mouths of the Danube.

Most of the natural salt pans on the Black Sea coast have been much modified by man, and extensive salt works are in existence. The process is by solar evaporation during the dry months of the year. The most productive and most numerous of these salt pans and limans are found in the Crimean peninsula, where the number of salt-producing pans, lakes, and marshes numbers many hundreds (see further Chapter XXXIV, Vol. II).

Other Salt Pans.—Natural salt pans are found on nearly all coasts where climatic conditions favor evaporation during part of the year. They are among the first sources of salt supply of all countries which border upon sea coasts.

Sea Shore Salt-pan Deposits Typically Fossiliferous

It is readily seen that wherever salt pans along the sea are fed directly by inflowing sea water at high tide or during periods of annual floods, some of the organisms which inhabit the sea will be carried into the salt pan, there to die on the concentration of the water under evaporation. Deposits formed under such conditions will, therefore, be fossiliferous and since the organisms die before precipitation of even the gypsum takes place, their remains will generally be found at the base of the successive gypsum layers or in the fine mechanical sediment which underlies these gypsum beds. Here then is a definite criterion by which salt deposits of this type may be recognized if preserved in older rock series. Moreover, normal marine deposits are forming simultaneously in the immediate vicinity of the salt pan, and should be associated with such a deposit formed during an older geological period.

Salt-pan Deposits Never Very Thick

A second characteristic of salt pan deposits is their relatively slight thickness, for it is obvious that unless local tectonic movements are taking place, which involve the salt pan as distinct from the supply basin, the thickness of the deposit which can be formed in it will be determined by the original depth of the pan. This from the nature of the case can never be very great, a few meters at the most may be set as the limit of salt deposition under these conditions.

Salt-pan Deposits Characterized by Gypsum

As normal evaporation of sea water produces at first deposits of gypsum, that mineral must be a common accompaniment of sea margin salt-pan deposits. Indeed, in some salt pans, where the water is not allowed to evaporate sufficiently before it is again diluted by a renewed influx from the sea, gypsum alone is deposited as in the case of the lagoons of some of the small coral islands of the Pacific, where it has been found to reach a thickness of 2 feet. In the artificial salt industry the gypsum is commonly allowed to crystallize out in separate pans. This may also be the origin of some older gypsum deposits unassociated with salt. As we have seen, the salt pans along the coast of the Red Sea are characterized by the regular alternation in the deposits of gypsum and salt.

Mother Liquor Salts of Salt-pans

The mother liquor salts are deposited when complete evaporation takes place, and they would naturally be formed in the salt-pans which become completely dry after each inundation. The amount of such salts is, however, extremely small, and would never be sufficient for purposes of exploitation. Most commonly, however, complete evaporation does not occur, the mother liquor remaining in the minor pools or covering the salt surface as a thin sheet of bitterns.

B. MARINE SALINAS

The name marine salina is here given to a salt lake or salina near the sea, the water of which is supplied from the sea, not by overwash or canals, as in the case of the salt pan, but by underground passages such as seepage through the sand or other material which separates it from the sea. Such salinas have not only a distinctive character (comparable in many respects to inland salinas) but their deposits will be of a distinctive type, differing from that of the salt-pans both in character of material and in the absence of organic remains.

The Salt Lake of Larnaca, Island of Cyprus

On the Island of Cyprus in the eastern end of the Mediterranean is a remarkable salt lake which may serve as a type of sea salinas, a step removed from the salt-pan type. This salt lake lies about a mile to the southwest of the town of Larnaca (or Scala) on the southeastern side of the island. It has been fully described by Bellamy,[1] from whose article the details are taken (Fig. 56).

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[1] C. V. Bellamy, " A Description of the Salt Lake of Larnaca," Geol. Soc. London, Quart. Jour., Vol. 56, pp. 745-758, 1900.

The lake, which lies in the lowest part of an irregular basin about 22 square miles in area, has a superficial area of about 2.1 square miles. It is separated from the Mediterranean by a low, flat barrier, from a mile to a mile and a half in width, and covered with low brush-wood except for patches of barren ground, which in winter are covered by a few inches of fresh, brackish, or salt water. The greatest depth of the lake is only about 3 feet, and in winter its surface is seven feet below the surface of the sea. A cross-section is shown in Fig. 57.

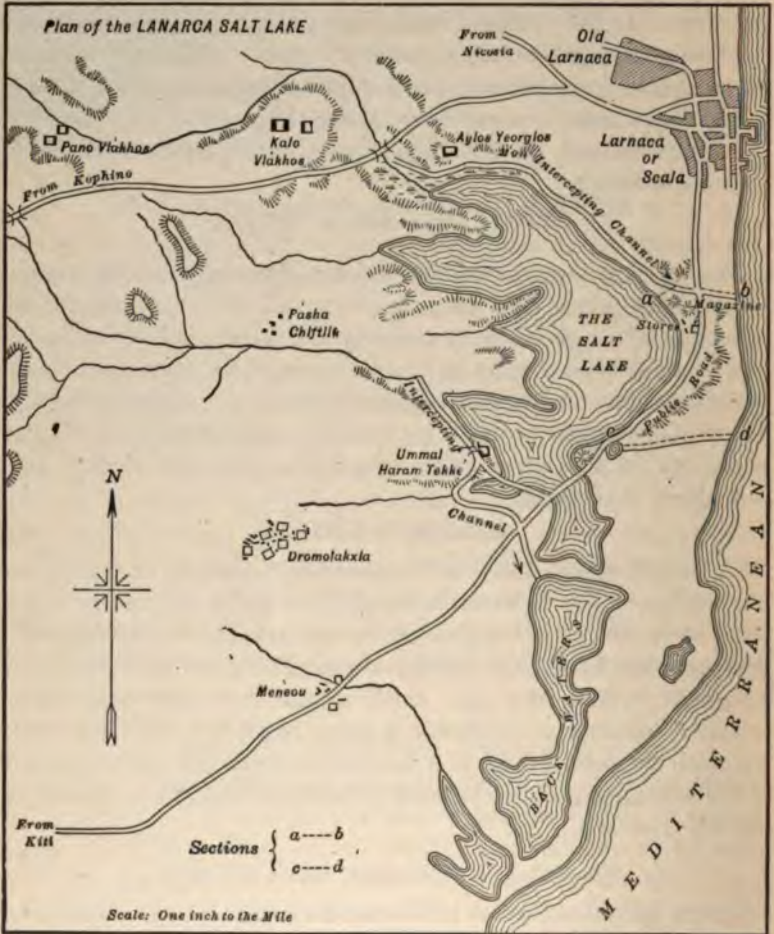

FIG. 56.—Map of the Salt Lake of Lanarca on the Island of Cyprus. (*After Bellamy.*)

A boring made in the barrier under the direction of Mr. Bellamy, revealed the following section in descending order:

1. Yellowish calcareous or shelly sand	12–18 inches
2. Black mud similar to that found in the lake	6–12 inches
3. Shelly layers and sand and conglomerates, with fine plastic impervious lime-mud in places	8 feet
4. Soft, plastic lime-mud with much salt water	2 feet
5. Stiff, calcareous clay	12–15 feet
6. Hard, impervious basal bed	

Ten days after the hole was made, it was found filled with salt water which had risen from the pervious layer (No. 4). The density of this water was more than twice that of the sea water, and about 75 per cent. that of the water of the lake at the time of observation. It is through this layer and perhaps to some extent through the overlying layers as well, that the sea water percolates into the basin of the lake, which, as has been noted, lies below sea level. The rate of inflow is so slow, however, that no water accumulates in the lake during the intensely hot summer months, the salt merely forming as an efflorescence or encrustation over the lake bottom. In winter, however, when there is less evaporation and more precipitation, water accumulates in the lake basin.

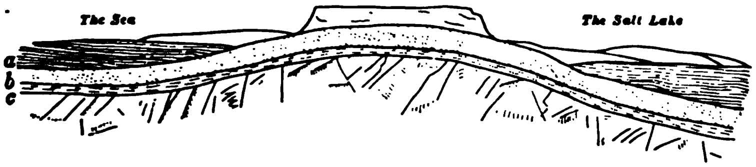

Fig. 57.—Cross-section of the bar separating the Lanarca Salt Lake from the sea. a, Permeable stratum of sands and pebbles. b, Layer of watery matter. c, Impervious stratum (clay).

Formerly the rainfall over the entire basin of 22 square miles entered the lake, but most of this has now been diverted by channels to the sea. If all the drainage of the catchment basin surrounding the lake were carried into it, the lake would be filled more than twice over, and it is probable that in spite of the extensive evaporation during the summer little or no salt would be deposited.

The salt encrustation rests upon a layer of mud, full of the decaying remains of microörganisms, but from the nature of the case no marine organisms are carried into this lake. The barrier, however, abounds in organic remains and is of comparatively recent origin, for in Tertiary time the basin in which the lake lies was an arm of the sea.

Salt of excellent quality has been gathered from this lake since the 16th century, and as there is a constant supply this will continue as long as the barrier exists. In 1904, 3,954 metric tons were produced on the island. Mother liquor salts seem not to be deposited, remaining probably in the water of the pervious layer. Even if the salt were not harvested annually, it is evident that no great thickness could accumulate since the depth is limited by the depth of the basin.

Other Examples of the Larnacian Type

Salt lakes of the Larnacian type are probably not uncommon, though they have not been studied in such detail. One is found in Cuba, near the Chaparra sugar estate, where the salt basin is separated from the sea by a barrier about half a mile in width, through which the sea water filters at the spring tides. Evaporation then leaves a crust of salt, mostly of a pinkish tint, which is raked up and harvested.[1]

The famous salt lake near Cumana on the peninsula of Araya, Venezuela, discovered in 1499, was of this type, being separated in the early days by a barrier above the level of high water, through which the sea water percolated. In 1726, however, during a hurricane of great violence, the sea broke through the barrier and converted the salt lake into a gulf several miles in length. At the present time the barrier is in process of reconstruction, the lake ordinarily being unconnected with the sea. As a result, this lake is returning to its former importançe as a source of salt for Venezuela. After a long time without rain, the greater part of the lagoon becomes dry, water from 3 to 5 feet deep remaining only in the deeper parts. The salt is harvested during the night on account of the intense heat on the peninsula during the day.[2]

A final example of the Larnacian type may be noted. This is Lake Tekir-Ghiol in Roumania, which is closely adjacent to the Black Sea, and separated from it only by a barrier, 300 to 400 meters wide. The area of the lake is 1,140 hectares, and its water has a salinity of 70.877 permille and contains mainly the alkaline chlorides, the other constituents of the sea water being present in less than normal amount. This is shown by the following analysis (Clarke). According to K. Natterer[1] the composition of such water may be explained by different diffusibility in the waters, so that in their passage through the barrier the more diffusible alkaline chlorides would be partially separated from the less active calcium and magnesium salts and so reach the lake in greater quantities than these.

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[1] Harris, *Loc. cit.*, p. 116.

[2] Von Buschmann, "Das Salz," Vol. II, 466, 467.

TABLE XXII.—COMPARISON OF ANALYSES OF WATERS OF LAKE TEKIR-GHIOL AND OF THE BLACK SEA

	Lake Tekir-Ghiol	Black Sea
Cl	60.53	55.12
Br	0.18	0.18
SO_4	0.67	7.47
CO_3	Trace	0.46
NO_3 and NH_4	Trace	
Na	34.78	30.46
K	1.68	1.16
Ca	0.28	1.41
Mg	1.84	3.74
Al_2O_3 and Fe_2O_3	0.03	
SiO_2	0.01	
	100.00	100.00

Characteristics of Ancient Deposits of the Larnacian Type

That salt deposits of this type were formed during the past geological history of the earth and are now buried in the rocks, is highly probable. We should not expect such deposits to be of great thickness and in character they would correspond closely to the salt-pans, except that the regular deposits of gypsum would be absent. Moreover, no organic remains occur in this salt except where, as in the case of the Araya basin, the sea momentarily breaks through the barrier, when during its occupancy a normal marine deposit is formed over the preceding salt bed, should this have escaped solution by the formation of an impervious covering stratum before the ingress of the sea. This

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[1] Monatsch. Chemie., Vol. 16, p, 666, 1895.

Larnacian type would, however, resemble the salt-pan deposit in that it would have associated with it a contemporaneous normal marine deposit, separated from the salt bed only by a comparatively narrow barrier.

No examples of ancient salt deposits of this or the salt-pan type are at present known.

C. LAGOONAL DEPOSITS

The sea margin deposits in natural salt pans and Larnacian basins can never result in the development of extensive salt deposits such as are found embedded in the older rocks. Moreover, it is evident that the preservation of such salts along the sea coast is often precarious, for the breaking of the bar and the influx of the sea into the basin would as a rule again destroy the small deposit of salt already formed.

The Bar Theory of Ochsenius.—To arrive at a conception of the origin of extensive and thick salt deposits, the German chemist, Professor Dr. Carl Ochsenius of Halle, developed in 1877 and 1878 the theory of salt deposition behind a permanent bar through which a constant or intermittent connection between the main water body and the enclosed lagoon behind the bar is maintained. The main elements of the theory were originally suggested by G. Bischof, but to Ochsenius belongs the credit of working it out in detail and of applying it to the elucidation of older salt deposits.

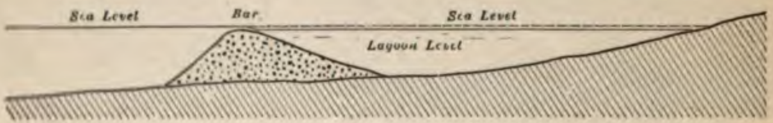

Fig. 58.—Diagrammatic section of a bar and salt lagoon. The difference in level between the sea and the lagoon is greatly exaggerated.

The bar in Ochsenius' view (Fig. 58) may be either orogenic or of wave or current construction, but must be a nearly continuous barrier which separates the lagoon from the main salt-supplying body, whether this be the ocean or a subsidiary water body. The basin of the lagoon must be of sufficient depth to permit the accumulation upon its bottom of a salt bed, of some thickness, the lagoon in this respect differing from the salt pan.

Moreover, the lagoon is permanently supplied with water through one or more breaches in the barrier, and normally does not suffer periodic dryings and floodings, as do the salt pans, though Ochsenius holds that complete drying up, with the deposition of the mother liquor salts, is the final fate of the lagoon.

The inlet or inlets across the bar must be sufficiently narrow and shallow to preclude a regular interchange of the waters between the lagoon and the main body, such as that which exists between the Mediterranean and the Atlantic across the Gibraltar ridge. Here the lighter Atlantic water flows inward to the Mediterranean as a constant surface current, while the denser water flows outward across the same barrier but at a depth of 400 meters.

The constant inflow of water into the lagoon is due to the lowering of the level of the lagoon by excess of evaporation over that of the supplying body. Since the inflowing current carries a constant amount of salt, it is evident that the salinity of the water in the lagoon is progressively increasing, for a uniform amount of salt is constantly added, while the quantity of water remains the same or slowly decreases. It thus appears that the salinity will finally reach the point where separation of salt takes place. At first gypsum will be deposited, and only when the salinity has reached or exceeded 388 permille will ordinary salt begin to separate out.

Under the postulated conditions, the constant influx of normal sea water would augment the supply of calcium sulphate as well as that of the other salts. As this salt is separated first, there must be a region of gypsum deposition near the entrance to the lagoon, while gypsum would accompany salt deposition in the main part of the lagoon as well. If no further supply of water were received, all the gypsum would after a while be deposited, whereupon only pure salt (NaCl) would be separated. This, Ochsenius assumed, is brought about by the closing of the inlet across the bar, which would be followed by a rapid increase in salinity of the water of the lagoon, and he attempts to explain pure salt beds like those of Wieliczka in this manner. A renewed incursion of the sea water would result in a dilution of the water of the lagoon and the cessation of salt deposition, followed by the resumption of deposition, first of gypsum and later of the sodium salt. If the incursion of the sea water brings with it mechanical sediments, a layer of these will first form over the last salt deposit, after which gypsum and then rock salt is deposited. Complete drying of the lagoon would result in the deposition of the mother liquor salts as the final chemical contribution. As these constitute approximately 22 per cent. of the entire solid (though the potash salts alone constitute less than 1.5 per cent. of the total), it would appear that for every deposit of gypsum and salt 78 feet in thickness a bed of mixed mother liquor salts about 22 feet thick should be formed.

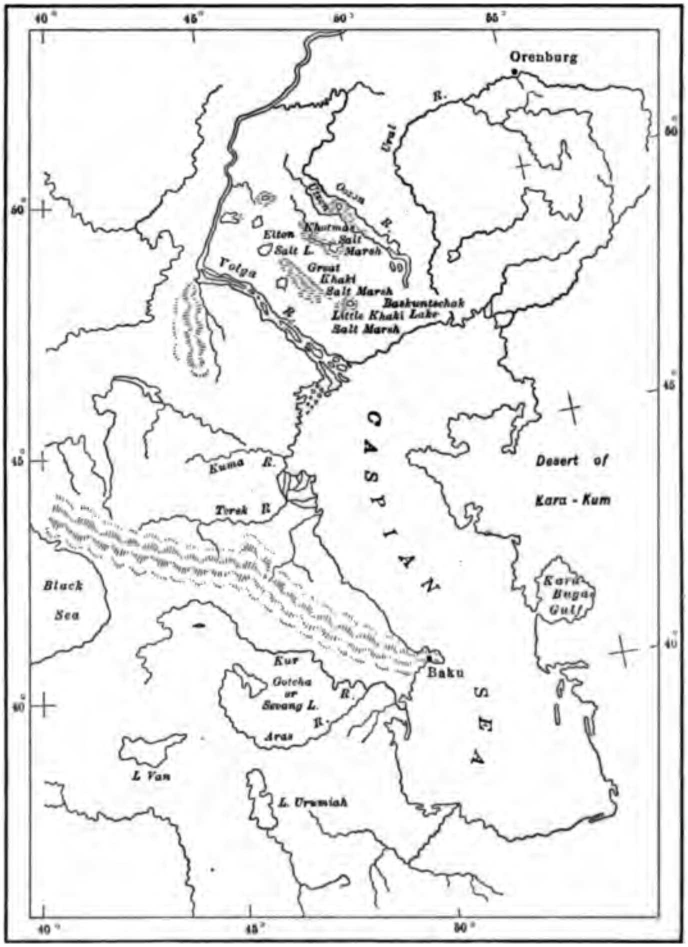

FIG. 59.—Outline map of the Caspian Sea with the Karabugas Gulf, and the salt plains of southern Russia.

The Karabugas (Adji-Darja) Gulf as an Example of a Salt Lagoon

In searching for a modern example to fit the requirements of his bar theory, Ochsenius met with partial success in the case of the Karabugas Gulf in West Central Asia on the eastern side of the Caspian Sea (Figs. 59, 60), and this he selected as his type illustration. This water body is an embayment of the Caspian Sea, lying between latitudes 40°30′ N, and 42° N, and is completely surrounded by desert country on three sides.

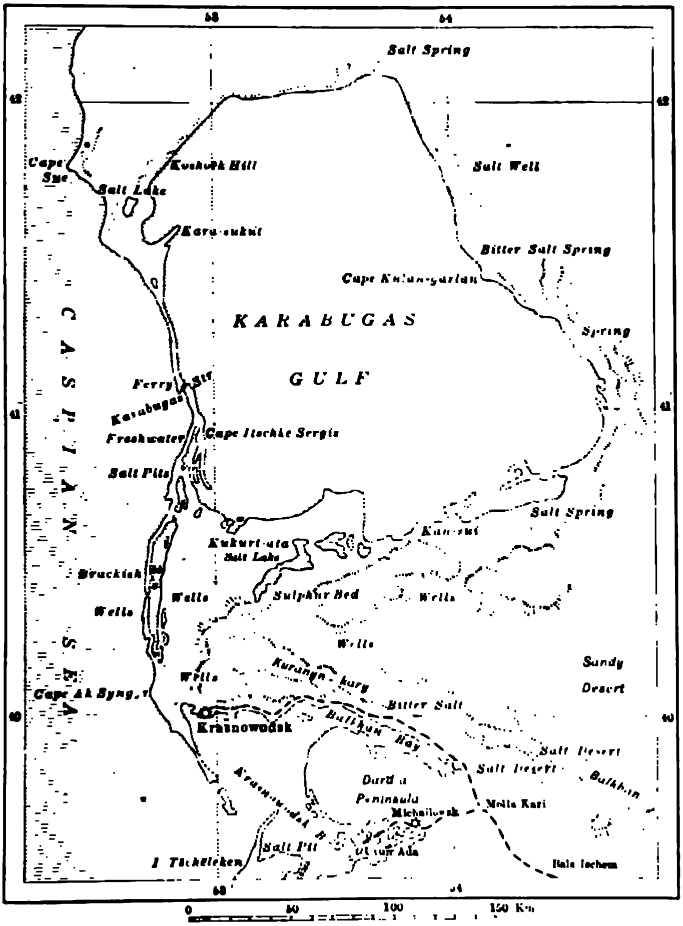

FIG. 60.—Map of Karabugas Gulf. (*Modified after Seidlitz.*)

It has a north-south diameter of 156 km., and a west-east diameter of 139 km. Its area is about 18,350 square kilometers, and the average depth is not over 15 meters, this increasing toward the Caspian. It contains about 183,000 million cubic meters of water, with a total salt content of about 34,000 million metric tons (Fig. 60).

The bar which separates it from the Caspian (Fig. 61) appears above the water as two narrow sand spits, one from the north, the other from the south, separated by a narrow and shallow strait extending north-eastward from the Caspian and having a length of 5 kilometers and a width varying from 100 to 500 meters. The name Karabugas, meaning black throat, refers strictly only to the strait, the gulf itself being called Adji-darja, or salt water.

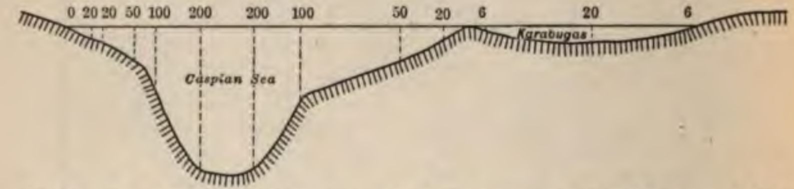

FIG. 61.—Section from Baku across the Caspian sea and the Karabugas Gulf showing the relative depths. Vertical scale much exaggerated.

Frequent changes in the conformation of these sand spits and in the width and form of the inlet have taken place, some of these being shown on the accompanying sketch map (Fig. 62) of the inlet at three successive periods, as given by the Russian geologist, Professor N. Andrussow.[1] The current passing through these straits always flows in the same direction in the winter as well as during the summer. The measured rate of flow was November, 24.7 meters, December, 25.9 m., January, 36.6 meters, February, 43.9 meters, and March, 41.8 meters per minute. In summer, when the level of the gulf falls, it is still greater. Between November and March the average quantity of water carried into the Karabugas was 1.07 million cubic meters per hour. This stream carries into the gulf a daily load estimated at 350,000 tons of salt. It also builds a delta in the gulf after the manner of an ordinary stream.

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[1] Andrussow N., 1897, Der Adschi-darja oder Karabugas Busen. Petermann's Mittheilungen, Bd. XLIII, pp. 25–34.

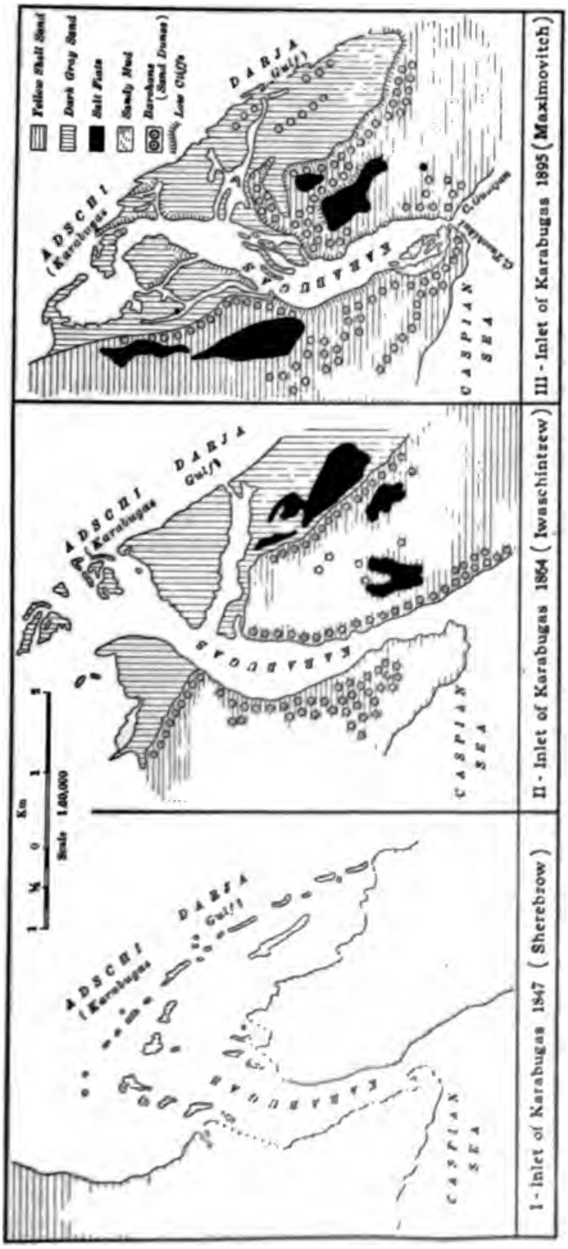

Fig. 62. Changes in the inlet to the Karabugas Gulf. (After Andrussow. *Petermann Mitteilungen*, Bd xliii, pl. 4.)

The level of the Caspian Sea, which is really a salt water lake, equalling in superficial extent about 1¾ times the combined area of the Great Lakes of America, lies 26 meters (85 feet) below the level of the Mediterranean.[1]

The exact level of the Karabugas Gulf has not been ascertained but is slightly below that of the Caspian. It oscillates regularly to the amount of four or five feet during the year, rising in winter and falling in summer. In spite of the sub-sea level of the Caspian, its salinity is below that of the ocean of which it is believed to have formed a part during a former geological period, as is especially indicated by its relict marine fauna. The average of 5 determinations of the salinity of the Caspian waters made in 1878 was 12.940 permille, its density being 1.3°, on the Baumé scale, while that of the Karabugas waters was 285.000 permille, its density ranging from 22 to 23° on the Baumé scale. The low salinity of the Caspian Sea may be accounted for by the constant influx of fresh water brought by the Volga, the Ural, and other rivers from the north. The Volga, with a drainage area of 592,300 square miles, characterized by an annual rainfall of 152.384 cubic miles, has a mean annual discharge of 43.736 cubic miles of water, or nearly one-third that of the Mississippi, which has a drainage area of more than twice that of the Volga, and is characterized by an annual rainfall of more than four times that of the Volga basin. With such a supply of fresh water, the evaporation over the basin of the Caspian must be considerable to keep its level below that of the sea, but this does not afford a final explanation of the small amount of salt in the water of the Caspian, the salinity of which is only about one-third that of the Mediterranean. If the Caspian once had the salinity of the sea, we must assume either that some of the original salt was carried out during a former higher stand of the lake, when its surface was above sea level, by the freshening effect of the river waters which entered it; or, what is more probable, that abstraction of the salt of the Caspian took place with the concentration of this abstracted salt in the marginal water bodies, like those of the Karabugas and others, and in lakes now entirely separated from the Caspian, like Tinetz Lake, the water of which has a salinity of 289.000 permille. Moreover, extensive salt deposits are found in the low lands bordering the Caspian, and which were formerly a part of this water body. Much, if not most of this salt, was undoubtedly abstracted from the Caspian during its shrinking, and probably represents lagoonal deposits formed on its borders at the various stages.

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[1] A variety of evidence seems to point to a considerable fluctuation in the level of this sea during historic time from an elevation of 120 feet or more above its present level in the 4th or 5th centuries before Christ, to about 20 feet below its level in the fifth and sixth centuries of our era, followed during the mediæval and modern periods by higher and possibly at one time a lower stand. Davis and Huntington record old shorelines at Baku and elsewhere extending up to 600 feet above the present level, and others, located a hundred miles east of the present coast on the line of the Central Asiatic Railroad, at an elevation of 150 and 250 feet above the present level of the Caspian. A rise of 144 feet would unite the Caspian with the Aral Sea, which lies 59 feet above sea level. Huntington concludes that these fluctuations are mainly due to variation in climate and consequent rate of evaporation, though a part of the rise in level from the beginning of the thirteenth to the middle of the sixteenth century was due to the inflow of a part, at least, of the waters of the Oxus River. (Huntington, Pulse of Asia, p. 350.)

In the following table a comparison of the analyses of the waters of the Caspian and of the Karabugas is given in percentages of total solids. In the consideration of these analyses the differ-

TABLE XXIII.—ANALYSES OF CASPIAN AND KARABUGAS WATERS, WITH OCEAN WATER FOR COMPARISON

	Ocean water	Caspian		Karabugas[1]	
		1878 C. Schmidt	1902 A. Lebedintsoff	1878 C. Schmidt	1902 A. Lebedintsoff
Cl......	55.29	42.04	41.78	53.32	50.26
Br......	0.19	0.05	0.05	0.06	0.08
SO_4.....	7.69	23.99	23.78	17.39	15.57
CO_3.....	0.21	0.37	0.93	....	0.13
Na......	30.59	24.70	24.49	11.51	25.51
K.......	1.11	0.54	0.60	1.83	0.81
Rb......	....	0.02	....	0.06	
Ca.......	1.20	2.29	2.60	....	0.57
Mg......	3.72	5.97	5.77	15.83	7.07
SiO_2, PO_4 Fe_2O_3....	....	0.03			
Total percentage..	100.00	100.00	100.00	100.00	100.00
Salinity in permille....	35.00	12.94	12.67	285.00	163.96

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[1] Foot note next page.

ence in salinity between the two water bodies must be kept in mind. The composition of normal ocean water is also given for comparison.

It will be observed that whereas the composition and salinity of the Caspian did not vary greatly in the two analyses, those of the Karabugas show a pronounced change. This may in part be due to the localities from which the waters were selected, for it is evident that both salinity and composition will be different near the entrance from that of the other parts. The density of the water is greatest in the center of the gulf and in its deeper portions.[1]

A comparison with ocean water shows especially the preponderance of the sulphates in the Caspian, as well as the greater amounts of lime and magnesia. This is in part, at least, accounted for by the composition of the water of some of its affluents. Thus the river Atrek, a western affluent of the Caspian, brings in water of 14.95 permille salinity, of which 43.09 per cent. is SO_4, 6.09 per cent. CO_3, 5.98 per cent. Ca, and 5.40 per cent. Mg. Cl is represented by 19.33 per cent. and Na by 19.03 per cent.

A more striking feature is the almost complete elimination of the calcium from the waters of the Karabugas and the corresponding high percentage of magnesia. The salinity given by Schmidt is in excess of that required for the precipitation of calcium sulphate, and his analysis shows that all calcium had been precipitated out. Gypsum forms in considerable quantity along the shallow shores of the Bar in the gulf, as well as everywhere along the shores of the gulf itself at a distance from the mouth of the strait. It forms a white crust of pure gypsum, or binds the sands along the shores into a solid rock mass. When the water level falls in summer, great stretches of flat coast covered by a black sand with numerous gypsum crystals and scattered shells of *Cardium edule L.* are exposed. Gypsum is also found near the margin where the salinity is less (16–17°Bé.), and farther in a bed of this salt occurs. During the winter months the water is saturated with respect to sodium sulphate, but not for the chlorides. In the warm season, however, the water is unsaturated, hence sodium sulphate (Mirabilite or Glauber salt, $N_2SO_4.10H_2O$) is deposited in winter time in the shallow waters along the shore, and toward the center of the Gulf. Here occurs a layer of this salt averaging one-third meter in thickness in summer, but increasing considerably in winter. Its area is estimated at 3,500 square kilometers, and the quantity of the salt at 1,000 million metric tons in round numbers.[1] This rich deposit is of less influence on the Russian industry than it might be, for which the unwholesome climatic character of the region is in part responsible.

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[1] Andrussow (*Loc. cit.*, p. 26) states that the measurements of the density of the Karabugas waters, made by P. Maximowitsch in the winter of 1895 and by himself in June, 1895, gave for the surface waters 16 to 17° Baumé. The higher density was obtained by Maximowitsch on January 21, 1895, two nautical miles south of the entrance of the strait at a temperature of +4°. At the same place Andrussow and Alfthan found the density to be 16°Bé. on June 30, 1895, at a temperature of 23.7°C., after a heavy northwest wind. On the shore about 30 nautical miles from the entrance of the straits, in water only one inch deep, they found a density of 17.5° Baumé at a temperature of 35°C. Andrussow doubts that the water analyzed by K. Schmidt (Column 4, Table XXIII) was derived from the Karabugas. It was gathered by a cossack sent out for this purpose, but he may have obtained it in one of the very saline lakes or bays upon the border of the gulf.

Common salt (sodium chloride) is not deposited in the Karabugas owing to the fact that its waters have not yet reached the proper state of concentration, but it is nevertheless evident that such deposits will be formed when the proper degree of salinity is reached. This may require a greater reduction of the amount of inflowing water under present climatic conditions by a narrowing of the inlet, but it is also possible that this condition can be reached under the present rate of increasing concentration. Von Buschmann thinks that it will require centuries to bring the water to the proper state of concentration at the present rate of evaporation. In any case, the Karabugas serves as the best known modern illustration of concentration of sea water in a lagoon behind a bar.

Organic Remains in the Karabugas Basin.—In developing his bar theory, Ochsenius fell into the error of assuming that organisms carried into this water body, by the persistent inflowing current, and finding the salinity of the water too high for comfortable existence would again leave the lagoon by the connecting straits, and that hence the deposits found in the lagoon would be entirely unfossiliferous. In this opinion he has generally been followed by subsequent students of salt deposits, especially in America,[1] who have generally been unfamiliar with the habits of marine organisms. An appeal to the facts in the case of the Karabugas reveals a strikingly different situation. The abundant relict marine fauna of the Caspian is carried into the gulf in a constant procession, but escape from this natural fish pond is prevented not only by the nature of the inlet and its constant inflowing current, and by the natural behavior of fish and other organisms, under such circumstances, but also by the fact that the great salinity of the water quickly causes the death of all organisms save, perhaps, the most extremely euryhaline types. Andrussow gives us a vivid picture of the destruction of the fish which are carried into the Karabugas during the spring and fall, and to some extent in the summer as well. "Their carcasses," he writes,[2] "float about as long as the water flowing into the gulf moves them, after which they either sink to the bottom or are driven onto the shores." The carcasses of *Clupea, Atherina, Cyprinus, Lucioporca, Acipensis,* and *Sygnathus*[3] piled upon the shores are partly eaten by the native birds, "and the quantities of dead fish which lie upon these shores in March can be measured by the fact that the gulls at this season of the year feed only on the eyes of the fish and do not even take the trouble to turn over the fish to get at the other eye."

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[1] This was erroneously referred to as a layer of Magnesium sulphate or Epsom salt, in "Principles of Stratigraphy," p. 354. See S. Kusnetzow, Die Glaubersalzbildung im Karabugas Busen, Zeitsch. prakt. Geologie, 1898, pp. 26–27.

The muscles of these fishes, dried upon the shores, show the characters found in artificially salted and dried fish, like those of the fisheries of the Volga. H. Maximovitsch observed that in spring whole swarms of herrings and many other fish were carried into the bay and even young seals entered with them. In the strong brine they become blind, are saturated with salt, and are finally cast ashore by the wind. They are used to some extent as bait by the local fishermen, and many of them are eaten by the natives. The immense quantity of the fish and other organisms buried in the mud of the shores may, according to Andrussow, constitute an important source of the naphtha found in that region.[4]

Many other organisms are killed in these waters and their remains embedded in the sediments and precipitates. Some of them, like the euryhaline mollusk *Cardium edule*, lived in the gulf before the waters became so concentrated as to deposit sulphate. The dead shells of this mollusk are found on the shores of the Karabugas in enormous numbers. Living in the waters at the present time are great numbers of the brine crustacean *Artemia* (Fig. 82, p. 241) and several algæ.

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[1] See especially Lucius Hubbard, Mich. Geol. Surv., Vol. V.

[2] Andrussow, N., 1897, Der Adschi-darja oder Karabugas Busen, Petermann's Mitteilungen, Bd. XLIII, pp. 25–34 (29).

[3] All genera of fish which inhabit the Caspian.

[4] Kusnetzow, Zeitschrift für Prakt. Geol., p. 27, 1898.

These facts clearly indicate that salt deposits formed in lagoons which are fed from large bodies of normal salinity like the ocean, or of enclosed bodies of reduced salinity but still supporting life, should be abundantly fossiliferous, the remains of the contemporaneous fauna of the feeding water body being abundantly preserved in the condensation deposits as well as in the accompanying clastic sediments. Moreover, here, as in the cases of the salt pans, these salt deposits are formed in intimate association with normal fossiliferous deposits without salt, which form in the neighboring feeding body. Conversely, the absence of such normal deposits in the neighborhood, especially when coupled with the absence of organic remains in the salt-bearing series itself, is ample indication that the salt in question could not have been formed in lagoons fed by water from the neighboring sea.

As will be more fully shown later, many of our older rock salt deposits which have generally been interpreted as formed under the conditions postulated by the bar theory, show neither organic remains enclosed within the series, nor are there contemporaneous normal marine sediments within reasonable distance of the salt deposits. They therefore cannot be interpreted as lagoonal deposits of sea salts. Even the North German (Stassfurt) salt deposits, for the explanation of which Ochsenius first developed his theory, do not satisfy its requirements; and, as has been shown by Walther, Erdman, and others, they must be explained in another way.

The Bitter Lakes of Suez. An Illustration of Salt Deposits According to the Bar Theory

We have, however, an example of a salt deposit which seems to fill all the requirements of the bar theory and may be used as an illustration of a nearly completed series of this type. This is the deposit formed in the Great Bitter Lake of Suez, and discovered during the building of the Suez Canal, the waters of which have, however, again completely dissolved the salt layers (Fig. 63).

The canal (see Fig. 54) was cut in 1861–1863, and in the center of the Great Bittern Lake which was traversed by it, a salt bed 13 kilometers long, 6 kilometers broad, and averaging 8 meters in thickness, was found. The thickness of the bed in the center of the lake was estimated at 20 meters. The salt deposit was composed of parallel layers of rock salt, varying in thickness and separated by layers of earthy matter and small gypsum crystals. A mass 2.46 meters thick consisted of 42 layers of salt and gypsum, these layers varying in thickness from 3 to 18 centimeters. They were separated by earthy layers only a few millimeters in thickness. At a depth of 1.47 m. from the surface, two strong layers of pulverulent gypsum were found, the first 0.112 meters thick, and mixed with silt; the second 0.07 meters thick and pure.

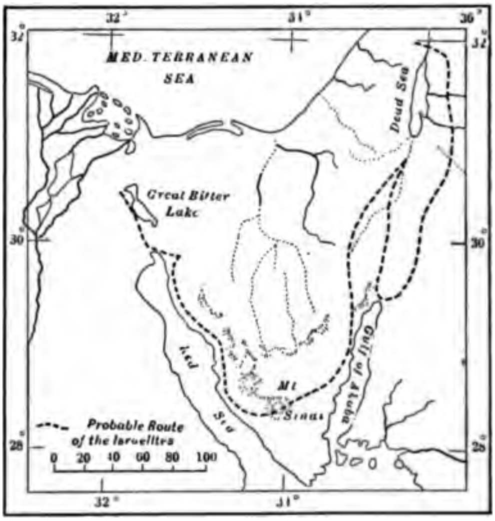

FIG. 63.—Outline map of the Sinai Peninsula, showing the location of the Great Bitter Lake and its relation to the Gulf of Suez arm of the Red Sea.

The numerous clay layers in the deposit were as a rule richly fossiliferous, containing the shells of marine genera and species of mollusks still living in the Red Sea. It is believed that before 600 B.C. these Bitter lakes of the isthmus of Suez formed a part of the present Gulf of Suez and the northern end of the Red Sea. The Gulf was known to the ancients as the Heroöpolitan Gulf, or Sinus Heroöpoliticus, and its northern end became separated from the present Gulf of Suez by the formation of a bar and the gradual silting up of the shallower portions adjoining it. It was probably across this forming bar, then only momentarily emerged at low water or during strong gales, that the Israelites escaped from Egypt to the Sinai peninsula, and that in its treacherous surface sands the pursuing armies of Pharoah were engulfed.[1]

While the connection between the lagoon and the rest of the Gulf still existed, concentration of the waters of the lagoon was going on under the influence of the desert winds, until the first of the salt beds was deposited. Repeated incursions of the sea freshened the water and permitted the Mollusca of the Red Sea to live for a time within the lagoon, while at the same time only clastic sediments were forming. Renewed concentration killed off the molluscan fauna, leaving their shells in the sediments over which first gypsum and later rock salt was deposited. The periodic renewal of these conditions, probably accompanying seasonal changes, caused the formation of the numerous alternating layers of fossiliferous silts, gypsum, and salt. Finally, complete closure of the inlet led to the precipitation of the last salt bed, whereupon only the mother liquor remained, which until 1869 still covered the salt bed, but was gradually removed by the passage of fresher waters.

The amount of bittern salts found in the mother liquor left over the surface of the drying lagoon until 1869 was less than would be required by normal evaporation, considering the amount of salt deposited in the lagoon. It must, therefore, be assumed that the successive inundations of the Red Sea, carried out a part of the mother liquor, then present, in diluted form, and that the quantity finally found, represented only that left from the last flooding of the lagoon. Since that time, when of course the level of the lagoon was that of the Red Sea, evaporation has been sufficient to lower the level of the lagoon to such an extent that two billion cubic meters of water were necessary to raise it again to the level of the canal.[1]

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[1] Here, at any rate, is where the Egyptologist Ebers places the crossing of the Red Sea, while Linant and Naville, and Dawson place the crossing over the Bitter lakes which at that time did not, of course, exist as separate bodies.

These facts at once suggest the unlikeliness of the preservation of bittern salts in lagoonal deposits. Indeed, as Walther has argued, complete evaporation of the mother liquor could only be brought about by the drifting over the lagoon of hot desert sands. These would remove the liquor with their salts by capillarity, the salts finally appearing on the surface as an efflorescence, whence they would be scattered far and wide by the desert winds.

So far as our observation goes, the older salt deposits bear out this theory. Fossiliferous salt beds, representing deposits formed in lagoons or otherwise in close association with the sea, have so far rarely furnished potash or other mother liquor salts. As an example, may be cited the famous deposits of Wieliczka in Galicia, which are abundantly fossiliferous, but carry no potash. They were probably formed in a lagoon in close association with the Miocenic sea, as will be shown more fully in a later chapter (Vol. II). An exception to this is seen in the Oligocenic deposits of Alsace, but these hardly represent a normal bar deposit.

The Modified Bar Theory of Branson

In the attempt to bring ancient unfossiliferous salt deposits into harmony with the requirements of the lagoonal theory of deposition of Ochsenius, Doctor E. B. Branson has recently suggested a modification of the bar theory, which consists in "supplying the receiving basin with highly concentrative waters instead of normal sea water."[2] As this theory applies to large evaporating water bodies which have become separated from the sea, its discussion properly belongs in another section (see beyond, p. 144). It is, however, possible to conceive the essentials of the modification as existing in the neighborhood of the shore, and therefore a brief reference is made to it here. Essentially such a modification had previously been proposed by M. Z. Kirk,[3] for the Permic rock salts of Kansas (see chapter XXV).

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[1] Ochsenius, C., Nova Acta, etc., Bd. XI, No. 4, p. 163.

[2] E. B. Branson, Origin of Thick Gypsum and Salt Deposits, Bull. G. S. A., Vol. 26, pp. 281, 282, 1915 (pp. 235, 236).

[3] Mineral Resources of Kansas, 1898, Salt, pp. 67–123 (89).

We may, with Branson, postulate the existence of two or more connecting lagoons, the first of which is separated from the sea by a bar with inlet, the others being separated from one another in a similar manner without, however, being directly connected with the sea. In the first lagoon the remains of the marine animals are buried, the saline waters preventing any of these from migrating into the second lagoon. Gypsum alone may be precipitated in the second (if not in the first) lagoon, while only the succeeding lagoons are concentrated enough to permit the deposition of salt, which would then be free from organic remains as well as from gypsum deposits. This is essentially the process employed in modern sea salinas.

It will be noted that this type of deposit when completed, differs from the normal single lagoonal deposit only in having the several products, the organic remains, the gypsum, and the salt separated. They would still be found in close proximity and furthermore they would also be associated with normal contemporaneous marine deposits. It would be a comparatively simple matter to determine from the character of a salt-bearing horizon, particularly from those portions outside of the salt area, whether these postulated characteristics are found. Without them, this modified theory likewise becomes inadequate as an explanation of a given salt, so far as direct derivation from the sea is concerned. No modern example of this type is known, and it might be questioned if such nice balancing of conditions could ever be maintained for any great length of time, so that the second basin would receive only waters entirely free from calcium sulphate.

CHAPTER VI

SALT DEPOSITS RESULTING FROM THE EVAPORATION OF THE WATER OF A CUT-OFF PORTION OF THE SEA

If within the belt of arid climatic conditions a subsidiary water body should be cut off from the oceans by the building of a clastic, or the development of an orogenic, barrier, such a water body would be doomed to extinction, provided that evaporation is not compensated for by renewed influx of water from the ocean or by sufficient precipitation and supply of fresh water by affluent rivers. Such a cut-off portion of the ocean isolates a certain amount of sea water which carries a definite quantity of sea salts, and these alone will form the deposit of salt on the final complete evaporation of this water. Moreover, the salt of the entire cut-off water body would tend to become concentrated in the deeper portions of the basin, for whatever crusts of salt are formed upon the floor of the basin as it becomes uncovered by evaporation, would again be dissolved by surface waters, even though these may be as infrequent as they are in some of the modern desert basins, where, as in portions of the Sahara, rain may fall at intervals of ten or even of twenty or more years. Thus the salt of a large water body becomes concentrated in a relatively small area or in a few depressions, and the deposit thus formed will be of proportionate thickness.

A HYPOTHETICAL EXAMPLE

We may illustrate this by assuming a body of oceanic water of 35 permille salinity, with a superficial area of 500,000 square kilometers, which is about that of the Caspian,[1] and an average depth of 100 meters, the basin thus containing 50,000 cubic kilometers of sea water. As one cubic kilometer of sea water contains 35,000,000 metric tons of salt, the total amount resulting from the evaporation of such a body would be 1,750,000,000 metric tons of salts, of which 77.758 per cent. is sodium chloride.

If we take the average specific gravity of the combined sea salts as 2.22, we have $\frac{175.00}{2.22} \times 10^{10}$ or 78.83×10^{10} cubic meters of salt. If this salt were concentrated over an area of 18,350 square kilometers, the approximate area of the Karabugas Gulf, it would produce a bed of uniform thickness of 42.95 meters.[1] If concentrated over an area over 1,000 square kilometers, somewhat less than the area of Lake St. Clair, Michigan, the deposit would be 788.3 meters thick, of which NaCl would form a series of beds aggregating 613.06 meters in thickness.

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[1] The area of this is more nearly 440,000 square kilometers, or 169,000 square miles.

In a basin of this type, the mother liquor salts are less subject to removal than they are in the basin previously discussed. From the size of the basin, there is little likelihood that they will be carried out even by winds. If they are scattered over the basin a subsequent moist period will cause their reassemblage in the central area. Moreover, wandering sand dunes are less likely to occur in the center of such a basin, and hence the mother liquor will remain until its salts are deposited by complete evaporation. That some of these salts require for their separation a very high temperature, such as is not usually found in nature, has been shown by the researches of Van't Hoff and his associates. Of the mother liquor salts found in the Stassfurt deposits, the following constitute a thermal scale or geological thermometer by which temperature conditions of the past may be measured:

1. Glauberite, $CaSO_4.N_2SO_4$, formed above 10°C.
2. Langbeinite $2MgSO_4.K_2SO_4$, formed above 37°C.
3. Loeweite, $MgSO_4.\ Na_2SO_4.2\frac{1}{2}H_2O$, formed above 43°C.
4. Vanthoffite, $MgSO_4.\ Na_2SO_4$, formed above 46°C.
5. Loeweite with Vanthoffite, formed above 60°C.
6. Kieserite with sylvite ($MgSO_4.\ H_2O + KCl$), formed above 72°C.

On the other hand, it should be noted that Kaleczinsky has measured temperatures of over 70°C. in natural salinas of Hungary, these high temperatures being due to the absorption of the heat of the sun by the dense layers of brine in the lower parts of the salt lakes. In Black Lake, for example, the surface temperature was 21°, while the deeper dense layer had a temperature of 56°C.[2]

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[1] The salt now contained in solution in the waters of the Karabugas Gulf is estimated at 34,000,000,000 million metric tons, or about 1/50 the above amount. It would therefore make a layer somewhat less than 1 meter thick, over the entire area of the Gulf.

[2] A. Kaleczinsky, Über die Hungarischen warmen und heiszen Kochsalzseen, Budapest, 1902.

THE SALTON SINK CONSIDERED AS A MODERN EXAMPLE

The Salton Sink or Coahuila Valley (also called the Colorado Desert) (Fig. 64) is a depressed basin at the head of the Gulf of California, from which it is separated by a barrier composed apparently throughout of detritus of river origin. The floor of the deepest part of the basin lies 273.5 feet below sea level, and a part of the deepest depression is occupied by Salton Sea, a saline lake formed by the overflow of the Colorado, into the valley, where formerly was only a dry salt plain. This last overflow was finally stopped in February, 1907, when the lake had attained a length of 45 miles, a maximum breadth of 17 miles, and a total area of 410 square miles with a maximum depth of 83 feet. The salt deposits which occupied the floor of the valley when first discovered in 1853 are now largely submerged. In 1848 the salt lake was three quarters of a mile long and half a mile wide, with a depth of about 1 foot (Emory). In 1892 it was a salt marsh, and at other times it was a bed of dry salt. A boring to the depth of 300 feet showed the following succession.

1. Black mud, resting on a crust of salt ($NaCl$ and $MgCl_2$), 7 inches.
2. Black ooze, with over 50 per cent. water, sodium and magnesium salts, fine sand, iron oxide and clay, 22 feet.
3. Hard clay with streaks of cement, 277 feet.

Salt was deposited here at one time at the rate of from 10 to 29 inches a day in the dry season. Brine from numerous salt springs in the adjacent hills flows into the depression, this brine being probably derived from salt which was deposited by the water at a former higher stand. The basin is bounded on the east, north, and west by mountain ranges, of which the western ones, the San Jacinto ranges of the Peninsula mountains, are effective as a barrier across the moisture-bearing westerlies from the Pacific. These winds, therefore, leave their moisture on the western slope of the coast range, crossing which they become drying winds with the result that the Salton basin, except where modified by irrigation, is a desert. A temperature of about 66°C. (130.8°F.) in the sun prevails.

From the general conformation of the region and the geological structure, it would appear that the Salton Sink was originally a prolongation of the Gulf of California, which, as has been noted in an earlier section, is a typical funnel sea, gradually shoaling headward. At that time, of course, the basin was filled with normal sea water, the level of which was one with that of the

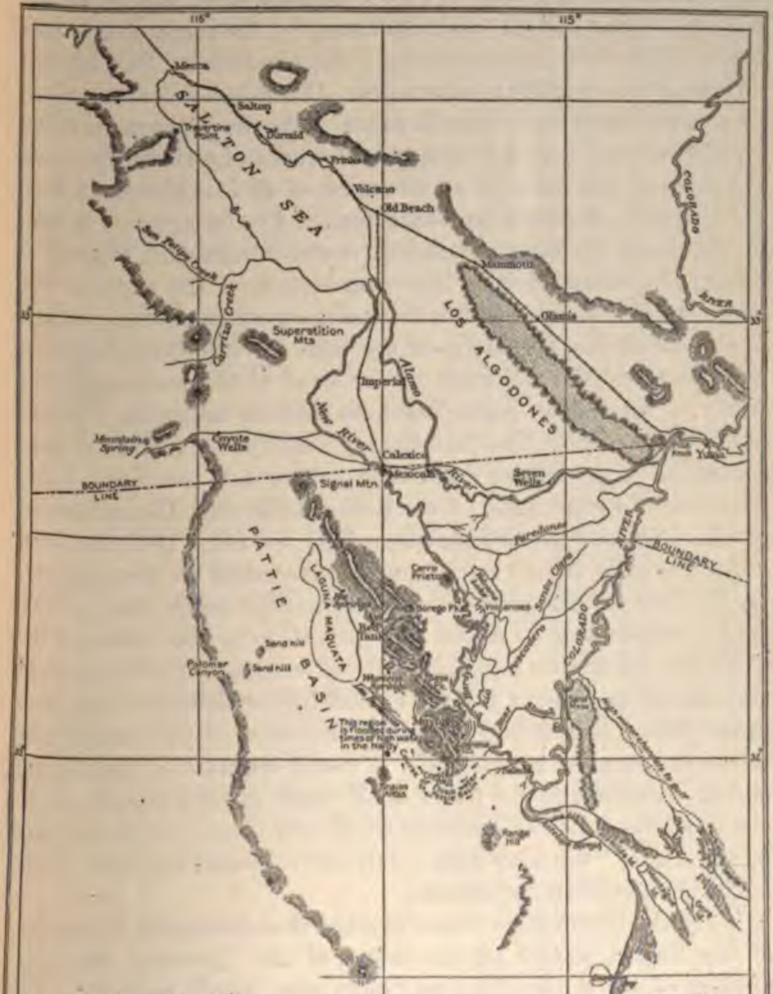

FIG. 64.—Map of the delta of the Colorado River including the Salton and Pattie Basins. (*Compiled and drawn by Godfrey Sykes. Am. Geog. Soc. Bull.* xxxix.)

ocean. The Colorado River, which entered this funnel sea from the east, some distance below its head, began to build its delta which grew to such a size that it finally extended entirely across the funnel sea, and cut off the head portion. The delta was built to a minimum height of 40 feet above sea level, and at first the cut-off portion had its water freshened by the inpouring into this basin of the river water, forming Lake Coahuila. This lake had an area of about 2,000 square miles. It was 100 miles long and its maximum width was about 35 miles. The fresh character of this lake is indicated by the existence of traces of a shoreline around the sides of the basin at an elevation of 40 feet above sea level, the deposits of which are characterized by the presence in them of the shells of fresh or brackish water Mollusca. Deposits of calcium carbonate left by the evaporation of the water at this stage are also found. Below this main shoreline are many others, made during the shrinking of the lake. With the deflection of the mouth of the Colorado to the head of the marine gulf, the water of the Salton basin began to dwindle under the influence of the drying westerlies, until the remnants of the water were concentrated in the deeper depression, where now lies Salton Lake. The rate of evaporation of the Salton Lake since the rediversion of the Colorado from February, 1907, to July, 1912, has been almost exactly 5 feet per annum. According to the engineer, H. T. Cory in charge of the rediversion, the entire lake will dry up by evaporation in about 18 years, if no further inflow of the Colorado River into the Salton Basin occurs. If all the salt of the original portion of the sea cut off by the delta still remained in the water, this should have been deposited in the central area as the evaporation progressed. A rough estimate of the amount of salt contained in the water of the basin gives a quantity sufficient to form a bed 12.5 meters thick over the area of the present Salton Lake. Whether such a salt bed underlies any part of the basin has not been ascertained.

It should, however, be borne in mind that during the freshening of the Salton waters by the influx of the Colorado, the total amount of salt in the basin may have been greatly reduced. For as long as the fresh water of the Colorado flowed in and the water of low salinity from the basin was carried out to sea, there was a constant loss of the original salt content. Thus when the outlet finally became inactive through lowering of the level by evaporation, only a small amount of salt may have been left in the water, and this alone would be deposited by complete evaporation on the bottom of the basin.

TABLE XXIV.—ANALYSES OF THE WATERS OF SALTON SEA AND OF OTHER NATURAL WATERS FOR COMPARISON. (W. H. ROSS, CARNEGIE INST., PUBL. 193, P. 45)

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
Na	31.29	33.14	19.75	25.64	26.67	14.43	30.59	33.39	24.70	13.39
K	0.65	0.30	2.17	1.87	1.26	1.95	1.11	1.08	0.56	2.37
Ca	2.80	1.37	10.35	7.30	6.43	14.78	1.20	0.42	2.29	4.79
Mg	1.81	1.55	3.14	2.50	2.61	2.05	3.72	2.60	5.97	11.85
$Al_2O_3 + Fe_2O_3$	0.02	.....	.....	.....	.....	4.63	.....	.....	0.03	traces
SiO_2	0.26	.....	3.04	4.66	2.93		.....			.....
Cl	47.83	52.62	19.92	32.68	40.71	13.55	55.29	56.54	42.04	65.22
Br	trace	trace	.....	.....	.....	.....	0.19	.....	0.05	2.08
SO_4	13.41	11.00	28.61	15.24	7.59	31.33	7.69	5.97	23.99	0.29
CO_3	1.83	.....	13.02	10.11	11.80	17.28	0.21	.....	0.37	0.01
Other constituents	0.08									
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity per mille	3.349	......	0.695	0.923	1.015	0.390	35.190	195.580	12.940	222.834

A – Salton Sea. Analysis of 1907 (after dilution by Colorado River Water).
B – Original Salton Sea. Supposed composition as calculated from excess of constituents of present lake in 1907 over that found for Colorado River.
C – Colorado River at Yuma, mean of seven analyses made at intervals of about 2 months, of samples collected almost daily between January 10, 1900 and January 24, 1901.
D – Gila River at head of Florence Canal, Arizona. Mean of four analyses of composites of samples collected daily for seven, five, four and five weeks, respectively, between November 28, 1899 and November 5, 1900.
E – Salt River at Mesa, Arizona. Mean of six analyses of composites representing samples collected daily for four, one, four, ten, thirteen, and eight weeks, respectively, between August 1, 1899 and August 4, 1900.
F – Rio Grande at Las Cruces, New Mexico. Mean of twelve consecutive monthly analyses of composites of samples collected daily from June 1, 1893 to June 1, 1894.
G – Ocean water, mean of 77 analyses by W. Dittmar, 1884.
H – Great Salt Lake. J. E. Talmage, 1889.
I – Caspian Sea. Mean of five analyses by C. Schmidt, 1880.
J – Dead Sea. F. A. Genth, 1859.

The salinity of the water of Salton Lake ranged from 7.348 to 7.164 permille in 1911. At 40 feet below the surface the salinity was 7.158 permille. In February, 1907, after the inflow of the Colorado was stopped, the range in salinity of the surface waters was from 2.588 to 3.418 permille, while at a point where the salinity at the surface was 3.382, at 10 feet it was 3.386, and at 30 feet depth it was 3.400. At another point where the surface salinity was 3.418, it was 3.386 at 10 feet depth, and 3.520 permille at 60 feet depth. There has thus been an increase in the density of the water of about 4 permille during the interval of 4 years, between 1907 and 1911, or at the rate of 1 permille per year. In the table on p. 149 the analyses of the waters of this lake are given with others for comparison.

The composition of the water (Anal. *B*) of the lake before contamination by the recent inflow of the Colorado, which, though of low salinity, is especially rich in sulphates (Anal. *C*), approaches that of normal sea water (*G*), though differing from that in the low potassium and magnesium content and in the higher percentage of sulphates. In some respects it is not unlike that of Great Salt Lake (*H*). It must be remembered that the Colorado water has entered this basin many times before, and that the lake water is to some extent modified by salts contributed from neighboring sources (see further Chapter XXXVII).

ALTERNATE HYPOTHESIS OF HISTORY OF SALTON SINK

According to Free,[1] the region was a desert valley and site of deposition of continental sediments, with gypsum and mirabilite in Tertiary time when the head of the California Gulf occupied only the lower part of this valley. He holds that the delta of the Colorado may have been built while the region stood at sufficient height above sea level to exclude the waters of the gulf, and that the Salton basin was never filled by the sea. The depression of the region may then have occurred after the head of the valley was cut off by the delta, the sea encroaching over the present area of the Gulf to the delta, but not entering the cut-off depression which was filled only by a fresh-water lake. According to this hypothesis, the salts of the basin are of purely connate origin. He admits that the fresh-water lake (Coahuila Lake, or Blake Lake) could not have formed prior to the depression of the valley relative to sea level, since the delta dam could not withstand a steeply graded overflow. He further admits that the delta of the Colorado was built into a body of water, but suggests that the sea may have slowly risen with the building of the delta. The absence of well-marked shorelines in the basin, such as would have occurred had this been a part of the sea, is taken as further proof of its exclusion throughout the history of the basin.

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[1] Salton Sink Report. p. 25.

It should be noted, however, that the salts of this lake can hardly be considered as of connate origin, as are those of Great Salt Lake, for no marine sediments which could furnish these salts are found in the vicinity. On Free's hypothesis one would rather expect these salts to be of the type found in the alkali playas of Nevada and eastern California (see beyond), which have a totally different character from those found in this lake at the present time.

CHARACTERISTICS OF DEPOSITS FORMED IN A CUT-OFF

If the Salton basin, then, be regarded at least as a reasonable illustration of salt deposition by evaporation of a cut-off basin, we may on the basis of such knowledge as we have of this region, deduce the criteria by which an ancient deposit of this type may be recognized.

In the first place, we may note that whatever deposits are formed in the shrinking waters of the basin, will be entirely unfossiliferous, because practically all animal life will disappear from the waters as soon as they become of abnormal salinity. Since, however, there can be no question regarding the presence of marine organisms in the original cut-off, for no marine water body is without its life, there must be a period, before the deposition of the salts begins when a widespread destruction of life occurs. This may be gradual, if the increase in salinity is a gradual one, for many animals are able to adapt themselves within limits to a changing salinity (euryhaline animals). As a result, we should expect the salt deposits to be underbedded by, or associated with, fossiliferous strata, in which the variety of organisms is greatest in the lower, and least in the higher strata, *i.e.*, those next to the salt deposit. This would be true of the succession of strata, even where the extinction of the normal oceanic fauna is brought about by a freshening of the water before desiccation sets in, except that here the final stratum would be characterized by the remains of brackish or fresh-water organisms.

It should be noted, however, that such regularity of succession is not to be looked for as a rule under the salt deposits themselves, since these represent the concentration of the salt in the central area of the drying-up basin, where in all probability only normal fossiliferous deposits were formed during the marine period of the basin. Thus the salt may come to rest directly upon normal marine deposits, separated from them by gypsum and, perhaps, by a series of clastic strata without organic remains. Somewhere within the basin, however, the graded series above referred to should be found, and this should pass upward into unfossiliferous deposits, which by their character, structure, and color are recognized to be the continental equivalents of the salt beds, and which were formed in the desert which surrounds the salt basin. Such desert deposits may be locally relieved by dry deltas and flood plains, of rivers which, on entering the basin dwindle away by evaporation. Such river deposits may include remains of the river faunas and flora, and temporary lakes formed during the rainy seasons may contain the peculiar crustacean fauna of desert lakes, especially the bivalved *Cypris* (Fig. 40, *G-J*, p. 98).

What is more significant, however, than the detailed character of the deposits within the basin is the fact that in this, as in the preceding cases, a normal marine series of contemporaneous sediments should be found in the neighborhood of the salt deposit. In the case of a cut-off like the Salton Sea, these deposits form only a comparatively short distance away in the Gulf of California. Where, however, the barrier which isolates a salt basin is of tectonic origin, being caused, perhaps, by the warping upward of a broad stretch of ocean bottom, the basin may become separated from the sea by a land barrier hundreds of miles in width. The Caspian, a cut-off which does not yet deposit salt, except around its margins, is separated by 500 miles of the mountainous tracts of Persia from the head of the Persian Gulf, by nearly 800 miles of mountain and desert from the eastern end of the Mediterranean, and by 300 miles of Caucasian uplands from the Black Sea. Yet in Tertiary time it was joined to the sea across one or more of those barriers.

Lake Tanganyika, in the great African rift valley, is 600 miles from the nearest point on the east coast of Africa, and 900 miles from the mouth of the Zambesi, along the probable line of the former connection. That the present Tanganyika is a relict of the sea is shown by the character of its fauna.[1] Its waters are fresh, or very slightly brackish, much of the original salt content having probably been washed out.

Though the separation of the cut-off from the main body may thus be a profound one, nevertheless marine conditions continue to prevail for a time at least within determinable distance of the salt deposit. Moreover, the character of the marine beds underlying the salt, corresponds to that of the lowest beds of the marine series outside of the salt basin, especially in the nature of its faunas.

As we have previously noted, basins of this type furnish the best opportunity for the deposition of the mother liquor salts provided they do not pass through a period in which salt is removed by influx of fresh water and simultaneous seaward drainage of the diluted salt water, as in Lake Tanganyika and apparently in the Salton basin. The mother liquor salts where deposited, will, of course, have a much more restricted distribution than the sodium chloride, becoming confined to the most depressed and last desiccated part of the basin. Moreover, it must not be overlooked that after the complete evaporation of the sea water and the deposition of the mother liquor salts, other salt deposits, especially of the desert type, may form over the marine evaporates, and these, as will be shown subsequently, will normally be without mother liquor salts. Thus all the normal salts of a region in which mother liquor salts have been found will not be associated with such deposits, and, indeed, the salts of the same vertical series may contain mother liquor salts in their lower part, but only normal sea salts (sodium chloride and gypsum) in their higher parts. The significance of this will be again pointed out in the interpretation of the salt deposits of the Stassfurt region in Germany, and of the Siluric salt deposits of North America (Vol. II). It may here be remarked, however, that it is hopeless to arrive at a proper determination of the origin of a given salt deposit without an exhaustive study of the entire formation in which it occurs. Thus the salt deposits of North Germany can only be understood when we have a comprehensive understanding of the Permic deposits and history of Northern Europe, while the understanding of the Siluric salt deposits of America requires a study of the Siluric deposits of the entire continent. The controversies even now waging regarding the history of these two important salt deposits, are more due, on the part of the contestants, to the lack of comprehensive knowledge of the formations in question, than to that of the details of the deposits themselves. That thorough understanding of the history of a deposit is essential to the most successful exploitation of the deposit, as well as to the location of new deposits of like character in the same or other formations is becoming increasingly apparent and cannot too strongly be insisted upon.

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[1] See "Principles of Stratigraphy," p. 1062, with literature references.

CHAPTER VII

CYCLIC SALTS

Oceanic salts which have been lifted from the sea with the spray, and have been blown inland, are known as cyclic salts, and their presence can be detected by the analyses of natural waters near the shore, from which they are derived. Near the sea coast the cyclic salt is abundant, inland it becomes small in quantity. In the following table, compiled by Clarke, are given the amounts of chlorine and chlorides brought to the surface by rain in different regions.

Table XXV.—Quantities of Chlorides Brought to the Surface of the Earth by Rain, in Pounds per Acre per Annum (for Bibliographic References See Clarke, p. 52)

Locality	Chlorine, pounds per annum	NaCl, per annum	Remarks
Cirencester, England	......	36.10	20 years' average.
Rothamsted, England	14.40	24.00	
Rothamsted, England	14.87		
Perugia, Italy	......	37.95	In 1887.
Ceylon	180.63		
Calcutta	32.87		
Madras	36.27		
Odessa, Russia	17.00		
Barbados	116.98	......	5 years' average.
British Guiana	129.24	195.00	20 years' average.
New Zealand	61.20	......	4½ years' average.

Joly has estimated that 10 per cent. of the salt found in solution in river waters must be regarded as cyclic salt, but Becker holds that 6 per cent. is a fairer estimate. A part of the cyclic salt is, however, retained by the soil, at least for a prolonged period of time; and wherever cyclic salts are carried to regions of inland drainage, an accumulation of salt beds may take place, the magnitude of which is determined by the quantity of salt brought into the region, and by the length of time during which the process has gone on.

SAMBHAR LAKE, AN EXAMPLE OF ACCUMULATED CYCLIC SALTS

An example of a salt lake produced in an inland drainage basin by the importation of cyclic salt, is found in the Sambhar salt lake in Rajputana, northern India[1] (see Fig. 53, p. 117). The enclosed drainage basin in which this lake is situated has an area of 2,200 square miles and lies more than 400 miles inland from the sea. When filled, the lake has a length of 32 kilometers (20 miles) and a width ranging from 3 to 11 kilometers (2–7 miles). It is very shallow, its greatest depth near the center after the heavy rains, is not over 3 meters, and for many months of the year it is less than 1 meter. The lake bed consists of parallel layers of clay and sand.

During the four hot and dry months of the year, dust-laden winds sweep over the plains which lie between this lake and the Rann of Cutch, bringing large quantities of saline materials from this coastal salt-pan and from the Arabian Sea. Analyses of the air during the dry season showed a quantity of salt carried in this manner, which amounts to at least 3,000 metric tons, over the Sambhar Lake annually, while the amount of salt carried into the Rajputana States annually in this manner is 13,000 tons.

The annual salt production from the waters of Sambhar Lake is in good seasons about 167,000 tons, which, as it exceeds the annual supply from the wind-borne salts, represents therefore the accumulated salts of many centuries. The highest production during the abnormally favorable year 1883–84, was 264,453 tons; the lowest, during the abnormally unfavorable year, 1892–93, was 3,371 tons. This was due to an unusually rainy period aggregating 104 cm., *i.e.*, 38 cm. more than the highest recorded previous precipitation. As a result, the salt formed was repeatedly dissolved again.

Three methods of salt production are in vogue,[2] the period of operation extending from November to May. (*a*) Within the basin have been built 10 permanently walled compartments called "Kyars," each of which is again divided into salt-pans 0.6 meters in depth. Here the water free from sediment is evaporated, yielding a coarsely crystalline salt of finest quality, which in good seasons amounts to 37,000 tons.

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[1] T. H. Holland and W. A. K. Christie, Records of the Geological Survey of India, Vol. 38, 1909, p. 154.

[2] Von Buschmann, Das Salz, Vol. II, pp. 44–45.

(*b*) Salt pans constructed of clay are built each year along the shores of the lake, additional ones being constructed as the shores of the lake recede with progressive evaporation. These pans are connected by run-ways from which the brine is pumped or ladeled into the higher salt pans. The salt here produced is of somewhat poorer quality and less well crystallized. In a half-way good season about 93,000 tons are produced.

(*c*) Residual salt is formed over the floor of the lake as this is exposed through evaporation. Such naturally produced salt averages 37,000 tons per annum.

The following analyses of the brine and salts of this lake were made from samples obtained during the winter of 1869–70 (Warth).

Table XXVI.—Analyses of Brines and Salts of Sambhar Lake

	A	*B*	*C*	*D*	*E*	*F*
	Brine of the lake	Brine from the pans	Mother liquor of the solar salt plants	Samples of crusts formed during salt production		
$NaCl$	22.4	18.2	19.7	24.5	9.5	18.1
Na_2SO_4	2.1	2.5	7.7	57.0	74.1	57.5
Na_2CO_3	0.4	0.5	3.1	11.0	12.8	10.6
Water	75.1	78.8	68.7	2.4	1.2	10.0
Insoluble Substances	....	....	....	1.8	0.8	2.0
	100.0	100.0	99.2	96.7	98.4	98.2

Warth has called attention to the small amount of water found in the samples of encrustation the analyses of which are given under *D* and *E*, from which he concludes that sodium sulphate can crystallize in an anhydrous state from saturated salt solutions without the application of artificial heat. The mother liquor contained a trace of bromine, but none of iodine. The natural salt obtained from this salt lake, when exposed to the sun, dries completely and becomes hard. At first it has a reddish tint, but later becomes very clear and of a good taste.

CHAPTER VIII

SALTS OF TERRESTRIAL ORIGIN, THEIR CLASSIFICATION AND CHARACTERISTICS

Under this designation we may include all salts which are deposited by terrestrial waters, by volcanic emanations, and by chemical reactions between deposits of salts already in existence in the earth's crust, as well as those due to complete or differential solution and redeposition of older salt deposits without chemical changes. Although it is probably true that in many cases chemical reactions complicate the deposition of salts from these several sources, it is well for purposes of discussion to keep the several types distinct. Accordingly we may classify terrestrial salts in the following manner:

I. Classification of Terrestrial Salts, Etc., According to the Source of the Material

A. ORIGINAL SALT DEPOSITS.

(a) *From Solution.*

1. *Connate Salts.*—Salts included in the pore space of older marine sediments.
2. *Re-solution Salts.*—Salts derived from the solution of older salt deposits.
3. *Decomposition Salts.*—Salts derived from the decomposition of other rocks (chiefly igneous) of the earth's crust.
4. *Magmatic Salts*—Salts derived from magmatic or juvenile waters.

(b) *From Vapors.*

5. *Volcanic Salts.*—Materials derived from the vaporous emanations of volcanoes and
6. *Atmospheric Salts.*—Salts derived from the material normally in vaporous solution in the atmosphere, such as snow and carbon. These are, of course, not strictly salts, but should be noted in a discussion of saline deposits.

(c) *From Fusion.*

7. *Igneous Salts.*—These include all the mineral species due to solidification from igneous magmas (chiefly silicates). They are not considered in this book.

B. SECONDARY SALT DEPOSITS

8. *Meta Salts.*—Salts derived by the chemical reaction between reagents (water, gases, etc.) and a salt deposit, or by the combination or interreaction of original salts in contact.

9. *Residual Salts.*—Salts or other substances left behind on decomposition of other substances and removal of certain constituents—Kaolin, Bauxite, etc.

According to the mode of deposition, we may classify terrestrial salt deposits in the following manner:

II. Classification of Terrestrial Salts, According to Cause of Deposition

1. *Concentration Salts.*—Salts formed by concentration of the solution containing them (evaporates) or by the condensation of vapor.

2. *Super-saturation Salts.*—Salts deposited from super-saturated solutions.

3. *Precipitation Salts.*—Salts formed as precipitates by reaction in a solution with an introduced reagent whether gaseous or in solution, with which a new, less soluble salt is formed.

4. *Elimination Salts.*—Salts formed by the abstraction of a special substance on the presence of which the solubility of the salt depends, such as CO_2 in waters holding calcium carbonate. The salts thus eliminated are not soluble to the same extent in pure water.

5. *Organic Salts.*—Salts precipitated by the physiological activities of organisms such as lime by fresh water Mollusca and algæ, silica by fresh water diatoms, carbon by plants. (The last two are, of course, not salts in the strict sense of the word.)

6. *Refrigeration Salts.*—Salts (chiefly silicates) resulting from the refrigeration of igneous magmas, also salts deposited from solutions as the result of changes in temperature (see Chapter III). Salts and other substances due to cooling of vapors, including sulphur, snow, etc., and ice resulting from the refrigeration of water.

The student must here be cautioned in drawing too sharp lines of distinction between these types. Organic salts may be deposited by the abstraction of the solving medium (CO_2) from water by the organism, or by the production of a reacting substance such as ammonium carbonate, which will cause the lime salt to be precipitated upon or within the tissues of the organism. Super-saturation again may be produced by concentration or by refrigeration of the solution. In general, however, the types here given may be considered as essentially distinct.

Terrestrial salts and saline deposits are far more varied in kind than are those of marine origin, and generally they are far more complex. Properly speaking, practically all the silicates belong in this category—those formed by the refrigeration of igneous magmas taking first rank. In terrestrial salts deposited from solutions in water, with which we are chiefly concerned in this book, the carbonates take first rank in point of abundance and universality of distribution. Carbonate of lime (with or without carbonate of magnesia) of organic as well as inorganic origin probably holds first place, and carbonate of sodium comes next. Silica, too, is widespread and may at times outrank the carbonates in abundance. Chlorides are abundant, especially as connate and re-solution deposits, and sulphates, especially those of sodium, are common. Nitrates and borates are probably in large part of terrestrial origin, though borates of marine origin are also known. Finally, there are many rare salts and salt-like substances, which are only known to have a terrestrial origin. Many of these cannot even be mentioned in a work of this kind. The student desirous of enlarging his acquaintance with them should consult Dana's "System of Mineralogy," and recent treatises on minerals (see also Chapter II). We shall confine ourselves to a consideration of the commoner types of salts and saline deposits, with the exclusion of the silicates, the metallic oxides, and sulphides, and others of a like character. (See the list of salts and saline minerals given in Chapter II.)

The processes by which salts of terrestrial origin are deposited from solution in water are essentially the same as those which obtain in the case of sea salts. Salt-pans and lagoons occur on the borders of lakes as on the border of the sea, indeed the type of the lagoon, the Karabugas Gulf, is situated on the borders of a lake, although the salt of that lake is mainly a sea salt, complicated to a certain extent by the addition of salts of terrestrial origin. The complete evaporation of a lake, the waters of which receive their salts entirely from terrestrial sources, brings with it the deposition of those salts, under the same laws which govern the precipitation of the salts of a marine cut-off, only the results, expressed in kinds and quantities of salts, will be different. Moreover, since different rates, and to some extent a different order of precipitation from that characteristic for normal sea water, prevail in the case of lake or other terrestrial waters, on account of the difference of composition both in kind and in proportions which characterizes such waters, the products will differ to a corresponding degree. While, therefore, it will not be necessary to discuss the methods of concentration, their results, as well as the derivation of the salts will claim our attention. As before, we will select typical examples so far as possible of the least complex character. Before, however, turning to the consideration of them, we may briefly outline the classification of natural terrestrial waters, from which most of the salts to be discussed are derived.

Classification of Terrestrial Waters According to Form and Location

Terrestrial waters include the following types

A. Surface Waters. These comprise:

1. *Static Waters.*—These are stationary bodies of water [illegible] permanent, or of intermittent character. The first [illegible] ponds, whether salt, brackish, alkaline, or fresh. The second [illegible] the swamps and playa lakes, the latter commonly [illegible] and evaporating largely or completely during the [illegible]

2. *Coursing Waters.*—The waters of streams and [illegible]

B. Subsurface or Ground Water

3. *Vadose Waters.*—Subsurface water above the water [illegible] the sinking in of surface waters including those of [illegible]

4. *Phreatic-seepage Water.*—Below the water [illegible] of the true ground water.

5. *Connate Waters.*—Original water salt or fresh [illegible] of older sediments and a part of the medium in [illegible] deposited.

6. *Magmatic or Juvenile Waters.* Waters [illegible] tion of emanations of deep-seated igneous [illegible] waters absorbed from the country rock are [illegible]

Classification of Terrestrial Waters According [illegible]

From the point of view of their salinity [illegible]

1. Fresh Waters—containing only [illegible] carbonate of lime—potable water.
2. Salt Waters—containing chiefly [illegible]
3. Alkaline Waters—containing car[illegible]
4. Acid Waters—containing fre[illegible]

Fresh waters are those wh[illegible] permille. Thus the salinity [illegible] that of Lake Superior is 0.05[illegible] into Brackish, Saline, and [illegible] Brackish waters are those [illegible] 10 permille,[3] while those [illegible] nated as sub-brackish. W[illegible] of salts are designated [illegible] sub-saline; and all those [illegible] 10 permille are the truly saline waters. Wa[illegible] salt content are designated super-[illegible] in which

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[1] M. O'Connell, Bull. [illegible]

[2] R. A. Daly, Gene[illegible] Economic Geol., Vol. X[illegible] No. 6, 1917, pp. 487 [illegible]

[3] M. O'Connell, *Loc. cit.*

the alkaline carbonates and sulphates predominate. Their salinity may be of any range.

A more precise classification on a chemical basis is as follows:

Classification of Terrestrial Waters on a Chemical Basis

Natural waters, including the marine, have been classified in the following groups by Clarke ("Data of Geochemistry," 3d ed., p. 201) but all of these types are also characteristic of terrestrial waters.

I. Chloride Waters. Principal negative ion Cl.
  A. Principal positive ion sodium.
  B. Principal positive ion calcium.
  C. Waters rich in magnesium.
II. Sulphate Waters, principal negative ion SO_4.
  A. Principal positive ion sodium.
  B. Principal positive ion calcium.
  C. Principal positive ion magnesium.
  D. Waters rich in iron or aluminum.
  E. Waters containing heavy metals, such as zinc.
III. Sulphato-chloride Waters with SO_4 and Cl both abundant.
IV. Carbonate Waters. Principal negative ion CO_3 or HCO_3.
  A. Principal positive ion sodium.
  B. Principal positive ion calcium.
  C. Chalybeate Waters.
V. Sulphato-carbonate Waters, SO_4 and CO_3 both abundant.
VI. Chloro-carbonate Waters, Cl and CO_3 both abundant.
VII. Triple Waters, containing chlorides, sulphates and carbonates in equally notable amounts.
VIII. Siliceous Waters, rich in SiO_2.
IX. Borate Waters. Principal negative radical B_4O_7.
X. Nitrate Waters. Principal negative ion NO_3.
XI. Phosphate Waters. Principal negative ion PO_4.
XII. Acid Waters. Contain free acids.
  A. Acid chiefly sulphuric.
  B. Acid chiefly hydrochloric.

Only a few of these waters are common, and there are many of an intermediate character which would not readily be placed in one or the other of the groups here given. As Clark says: "Mixtures cannot be classified rigorously," and the classification here given is confessedly a convenient, rather than a strictly scientific one.

CHAPTER IX

CONNATE SALTS; THEIR ORIGIN AND METHOD OF CONCENTRATION

Definition of the Term.—When marine sediments of any type are formed upon the sea bottom, a certain amount of the sea salt, mainly in a state of solution as sea water, is inclosed within these deposits, and unless subsequently removed from them by leaching or otherwise, remains there indefinitely. This salt, inborn, as it were, in the sediments, may be termed *connate sea salt*, just as the water originally included within the sediments has come to be known as *connate water* (Lane). This salt must be distinguished from salts produced by the decomposition of rocks, which is a secondary product, whereas the connate salt is an original or primary part of the sediment. The amount of connate sea water included in the marine sediments depends upon the pore space of these sediments, but this, as we shall see, gives no adequate measure of the total amount of connate salts included within these sediments. That connate salts form the source of many of the great salt deposits of the world is becoming more and more apparent as the history of salt deposits is being investigated, and it is one of the great achievements of Johannes Walther to have for the first time adequately brought to the attention of the geological world this important source of salt deposits (see especially Das Gesetz der Wüstenbildung).

The Pore Space of Rocks.—It is a familiar fact that all rocks, even the densest, are permeable to water, even though this permeability of a rock may be of very slight degree. The pore space of a rock may be defined as the fractional part of the mass, when completely dry, which is occupied by open spaces or voids.[1] It can best be determined by saturating the rock with water, *i.e.*, by filling all the pore spaces and then measuring the quantity of water thus taken up by the rock, and comparing its volume with that of the rock mass itself. Practically, the increase in weight of the rock after saturation is determined, and the quantity of water which caused this increase is calculated. For the methods employed in this process, the student is referred to the work cited above.

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[1] C. S. Schlichter, The Motions of Underground Waters. Water Supply Paper, U. S. Geol. Surv., 67, p. 16, 1902.

If a cubic meter of a rock, say a sandstone, holds on saturation one-quarter of a cubic meter, or 250 liters of water, the porosity of the sandstone is 25 per cent. If it holds only 1 liter, its porosity is one-tenth of 1 per cent. A series of investigations carried on for rocks of various kinds, shows that a remarkable variation exists in the porosity of even the same kinds of rock. The following table from Buckley gives a few of these.

TABLE XXVII.—VARIATION IN THE POROSITY OF BUILDING STONES OF WISCONSIN (BUCKLEY)

Kind of rock and locality	Average porosity of two specimens in per cent.
1. Granite from Montello, Wis.	0.237
2. Granite from Berlin, Wis.	0.384
3. Niagara limestone from Marblehead, Wis.	0.770
4. Sandstone, Ableman, Wis.	5.600
5. Niagara limestone, Wauwatosa, Wis.	6.400
6. Lower Magnesian limestone, Bridgeport, Wis.	13.190
7. Sandstone, Ashland, Wis.	20.700
8. Sandstone, Dunville, Wis.	28.260

The porosity of quartz sand usually varies between 30 and 40 per cent., while that of clay loams ranges from 40 to 50 per cent. Ordinary sandstones range from 5 to 25 per cent. in pore space, while compact limestone varies from 0.2 to 0.5 per cent. (absorption 1 to 5 per cent. by weight of water). The more porous limestones, however, have a pore space of 25 per cent. (absorption 10 per cent. by weight of water), and chalk has been credited with a pore space of 41 per cent. (absorption 20 per cent. by weight). A recent organic limestone from the Gulf of Naples had a pore space exceeding 35 per cent. (Walther), while recent sediments of the Mississippi delta, had, according to Hilgard, a pore space ranging from 23 to 61 per cent. As will be seen from the above figures, recently formed sediments have a higher pore space than rocks formed by the consolidation of such sediments. This is natural when we consider that a part of the pore space of a sediment is filled by the cementing material of the rock.

Recently formed organic limestones, too, have a pore space exceeding that of the older rocks of this type, for secondary deposition of lime in the pores of a rock is a natural proceeding after formation, especially when the rock has been raised to the level of ground water circulation, when the connate water is removed and the deposits of the vadose circulation takes its place.

The pore space of clastic rocks varies not only with the variation in size and form of the clastic particles, but also with their variation in arrangement. Actual size is of less importance than variation in size within the mass. A rock composed of grains of uniform size will have a larger pore space than one in which the grains vary, so that the smaller ones may fill in the spaces between the larger ones. Rounded grains will produce more pore space in a rock than angular grains. The arrangement, too, is important, for it is evident that more pore space results if the grains of uniform size rest directly one upon another, than if they alternate in position. Schlichter has determined that the minimum porosity of a mass of spheres packed in the most compact way, is 25.95 per cent., while the maximum porosity, when the spheres are superposed, is 47.64 per cent., there being practically no variation when large or small spheres were used, so long as they were of the same size in each case (Fig. 65).

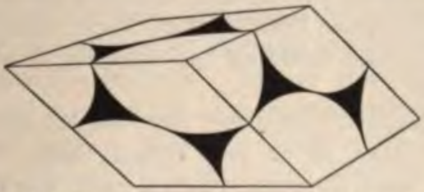
FIG. 65.—Diagram illustrating the pore-spaces in rocks composed of rounded grains. (*After Schlichter.*)

Amount of Sea Water Enclosed in the Pore Spaces.—In the determination of the amount of connate sea water enclosed within a marine deposit, the pore space of the rock at the time of formation must, of course, be taken. Hence our best information is to be derived from the determination of the pore space of recent deposits. As we have seen, Walther found the pore space of a recent marine limestone of organic origin to be over 35 per cent., while Hilgard found a pore space of 23 to 61 per cent. in the clastic sediments of the Mississippi delta.

If we take 30 per cent. as a fair average of the pore space of recent marine deposits, and take the average salinity as 35 permille, though on the bottom of the sea this is generally higher, and if we take the average specific gravity of the sea salt as 2.22, we would arrive at the conclusion that the average amount of sea salt included in marine deposits is about 1 per cent. by weight, or 0.47 per cent. of the volume of the rock. Of this, 77.76 per cent. is NaCl, which would amount to nearly 0.365 per cent. of the volume of the rock. From the foregoing, it would follow that a marine limestone with a pore space of 30 per cent. and a thickness of 1,000 meters would enclose enough salt to make a bed 3.65 meters thick, and covering the same area as the limestone. That limestone formations of this thickness and of vast areal extent exist, is well known. One need only mention the Jurassic and Triassic limestones of Europe, or some of the great Palæozoic limestones of North America, which are more than twice that thickness and extend over many thousands of square miles.

If the salt from a formation 100 feet thick, which covered 50,000 square miles, or an area slightly larger than the state of New York, were concentrated in a basin 100 square miles in extent or approximately the basin of Seneca Lake, it would form a bed 182.5 feet in thickness, and amounting to a volume of 3.45 cubic miles.

Connate Salts in Addition to Those of the Connate Waters.—It appears, then, that even if only sea water were enclosed in the pore spaces of marine deposits the amount of salt thus imprisoned in the rocks would be very great. Determinations of the salt content of modern marine sediments has, however, shown that the amount of connate salt is generally in excess of that which would be held by normal sea water within the pores of that sediment. Instead of 1 per cent. by weight, the amount sometimes ranges as high as 8 per cent. The following determination serves to illustrate this:[1]

Sediment	Salt content, per cent.
1. Deep sea red clay	6.8 to 8.0
2. Diatomaceous ooze	5.4
3. Antarctic glacial clay	1.9 to 3.7
4. Globigerina ooze	1.0 to 3.4

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[1] Karl Andrée, Ueber Sedimentbildung am Meeresboden, 1ster Teil., Geologische Rundschau, Bd. III, p. 355.

There seems thus to be an absorption of the sea salts, especially sodium chloride, by the sediments, rendering the salinity of the connate waters much higher than that of normal sea water.

According to this, we may safely double or triple the salt content of a sediment as indicated by the pore space, and hence decrease in the same proportion the thickness of the formation needed for the production of a given deposit of connate salts. Since marine deposits are of wide extent over the surface of the earth, and have been of even wider distribution in the past, it is evident that enough sea salt has been imprisoned in these deposits during the various geological ages to abundantly account for all salts which cannot be accounted for by the methods of direct precipitation from ocean water above discussed.

As it is now pretty certain that at one time or another nearly the whole of North America, including the greater part of the old crystallines which are now exposed, was covered by marine sediments during the Palæozoic, and as these sediments were probably seldom, if ever, less than several hundred feet thick in their thinnest portion, whereas in other parts they ranged up to eight or ten thousand feet (exclusive of the continental sediments), it is probably far below the mark if we assume that the marine Palæozoic strata were extensive enough to cover the whole of North America to the depth of 1,000 feet. On the basis of 0.365 per cent. of salt, enough connate salt was imprisoned in the rocks covering North America to make a uniform layer 3.65 feet thick over the entire continent. Much of this salt was, of course, again returned to the sea; but a considerable part of it was concentrated in the salt beds included in the continental Palæozoic sediments, as well as in the continental sediments of the succeeding periods.

Liberation and Concentration of Connate Salts.—When marine deposits, carrying connate sea water and salt in their pores, are elevated above sea level, they are brought into the zone of circulating meteoric waters, and this generally results in the leaching out of the salt and its dispersion by the streams. In regions of normal seaward drainage, such salt will eventually reach the sea again, but in regions of inward drainage the salt will be carried to the center of the basin and there left by evaporation of the water. Basins without outward drainage are found only in arid regions, for in regions of much rainfall all basins will be filled to overflow, the result being fresh-water lakes with outward drainage.

When the ground water level lies deep, as it generally does in desert regions, the connate water and salts can only be liberated by the disintegration of the rock which contains them, and by the drawing of the water to the surface under the influence of the intense heat of the desert sun. The water will, of course, evaporate, leaving an efflorescence of salt over the rocks, which is subject either to removal by wind or is redissolved by the occasional rain waters and carried toward the center of the basin, there to accumulate as a salt deposit.

THE TARIM OR LOP BASIN OF CHINESE TURKESTAN, AS A MODERN EXAMPLE[1]

In the heart of Asia, between the parallels of 30 and 50 degrees north latitude, lies the great desert belt of western China, which is indeed but a continuation of the deserts of the Aralo-Caspian region, and those of Turkestan. Of these the Takla-Makan desert in the basin of the Tarim River best serves our purpose, since it has an extended salt deposit in the Lop Plain, near its eastern end (Fig. 66).

The basin is a depressed block which lies between the Kwen Lun Mountain range on the south and the Tian Shan ranges on the north, these meeting on the west in the mountains of Pamir. Some of these mountains rise to heights of from 15,000 to 25,000 feet, and they are lofty throughout except at the northeast, where a comparatively low, maturely dissected mountain region separates the Tarim basin from the desert of Gobi. The area of the basin is equal to that portion of the United States east of Lake Michigan and north of Tennessee, or approximately three times that of Great Britain and Ireland. The drainage of the basin, where it does not die away in the sands of the desert floor, is toward the salt lake Lop-Nor, in its eastern end, the principal river, the Tarim, gathering in the streams from the western and northern slopes while a smaller stream, the Cherchen, carries a part of the drainage from the southern slope, the remainder withering away in the desert. The climate of the basin is determined by its position in the middle of the temperate zone, and in the center of the largest of the continents, as well as by the fact that it is surrounded by lofty mountain ranges, which shut out the moisture-bearing winds. The precipitation is thus very low, and the extremes of temperature very great. Some rain falls in the basin during June, July and August and a little snow during the winter months. The total annual rain-fall in the center of the basin does not amount to more than an inch or two. In the mountains, however, at an elevation of 10,000 feet or more, rain is plentiful and vegetation abounds.

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[1] Many of the facts here given are taken from Huntington's "Pulse of Asia."

The floor of the plain, which lies between 3,000 and 5,000 feet above the sea, appears essentially level and is a barren desert with little or no vegetation except along the streams, and covered with sand dunes of great height. This desert plain is 900 miles long by 300 miles wide, and is surrounded by a relatively narrow border of vegetation, developed where the streams from the mountains enter upon the plain and for the most part disappear by the evaporation of the water and its sinking into the thick deposits of sand and gravel. Outside of the belt of vegetation is a broad piedmont belt from 5 to 40 miles in width and sloping toward the plain. It is composed of the gravel brought by the streams from the mountains, and merges into the steeper slope of the coarse material dropped by the streams as they leave the mountains.

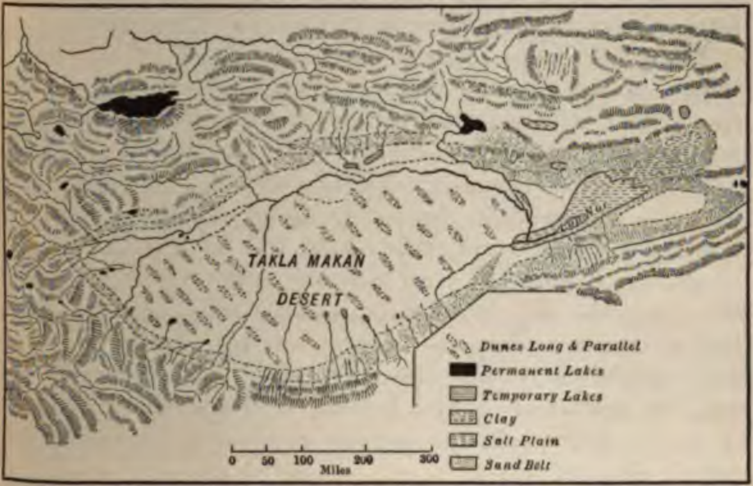

FIG. 66.—Outline map of Takla Makan Desert with Salt Lake of Lop. (*After Huntington.*)

In the eastern end of the basin lies the great salt plain of Lop, in which is situated the contracted modern salt lake of Lop-Nor or Kara-Koshun, which has an altitude of 2,600 feet above the sea. In places the piedmont gravel deposits border the plain, in others are vast stretches of desert sands and clayey loess which encroach upon its margins. The salt plain has a length of over 200 miles, with a width of 50 miles or over in its broadest portion. Large areas consist of solid white salt, with its surface "resembling the choppiest sort of sea, with white caps a foot or two high, frozen solid."[1] The salt is so hard that Huntington found that when he tried to drive his iron tent pegs into what appeared a soft spot, most of them bent double. He explains the roughness of the surface as follows (see Frontispiece):

"During the long-continued process of drying up, the ancient lake of Lop deposited an unknown thickness of almost pure rock salt. When the salt finally became dry, it split into pentagons from five to twelve feet in diameter, the process being similar to that which gives rise to mud-cracks when a mud-puddle dries up. . . . The wind, or some other agency, apparently deposited dust in the cracks, when rain or snow fell, the moisture brought up new salt from below, and thus the cracks were solidly filled. When next the plain became dry, the pentagons appeared again. This time the amount of material was larger, and the pentagons buckled up on the edges and became saucer-shaped. By countless repetitions of this process, or of something analogous to it, the entire lake-bed became a mass of pentagons with ragged, blistered edges."[2]

Faint broad hollows, a mile or two in diameter, are interspersed with the rough salt, and on these the surface is comparatively smooth and damp. Here the crust of salt rests upon an unknown depth of oozy salt muck, in which, according to local tradition, verified to a certain extent by Huntington's experience, men and camels may be swallowed up. These salt bogs, probably contain the more concentrated bitterns, which in spite of the prolonged drying process have not lost their water, owing to their greater resistance to desiccation. Unfortunately, nothing is known of the composition of these brines.

Clastic Deposits Associated with the Salts.—As already noted, the piedmont gravels encroach upon the salt plain in places, especially upon the south, there being, however, generally a zone of vegetation between the two. On the west the desert sands bound the basin, but on the north and east occur extensive deposits of loess-like clay, of red and green color and carved by the wind into mesas and tongues which extend into the basin. Beyond the salt plain, Huntington found: "A fantastic red plain, the soft dry bed of an older expansion of the lake [which] glittered with innumerable gypsum crystals, or was again sparsely studded with weird aeolian mesas from thirty to sixty feet high, made of horizontal layers of pink and greenish clay."[1]

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[1] Huntington, "Pulse of Asia," Chapter XII, Houghton Mifflin, 1907.

[2] *Loc. cit.*, pp. 251–252.

The salt lake or Kara-Koshun has, according to Sven Hedin, a depth of scarcely 2 meters. Its bed consists of fine, yellow mud which in turn rests upon black mud. Ten centimeters below the mud lies a bed of salt.

Organic Remains of the Salt Plain.—Obviously marine organic remains are entirely absent from these salt deposits, but those of terrestrial organisms are occasionally found. The Chinese tradition has it that travelers have become mired and completely buried in the softer salt muck deposits, and Huntington's experiences proved the ready possibility of this. Though animals in a state of nature avoid the salt plain, the possibility of such a miring of stray animals must not be overlooked. Huntington records the finding in the salt of a half-buried plover, dead for centuries, which was caught in the deposit when this was still soft. Elsewhere in the sides of a mesa, he saw the deeply buried roots of some reeds, which flourished when the lake had a greater expanse. On the whole, however, the entire series of deposits, saline as well as clastic, were essentially barren and no signs of life were encountered during a journey of nearly a hundred miles.

Source of the Salt of the Lop Plain. That the salt of the Lop Plain, is of connate origin can hardly be questioned. Unfortunately, we do not know enough of the geology of the enclosing mountains from the rocks of which this salt is derived, but we do know that among these rocks are Mesozoic marine limestones and other sediments. There are also great masses of Palæozoic limestones of Devonic and Carbonic age. The salts were probably in large part derived from the younger marine strata. Some of the older formations of the adjoining region carry salt, and such salt may form a partial source of supply for the Lop Basin.

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[1] *Loc. cit.*, p. 254.

THE KAVIR (KEWIR) DESERT OF PERSIA

The central part of Persia is for the most part a series of extensive deserts, that country being more or less completely surrounded by lofty mountain chains (Fig. 67). To the northeast of the ranges, which separate the interior from the Persian Gulf, lies the great Kavir Desert, also called the "Kewir," a name which signifies Salt Desert. This has been explored by Sven Hedin.

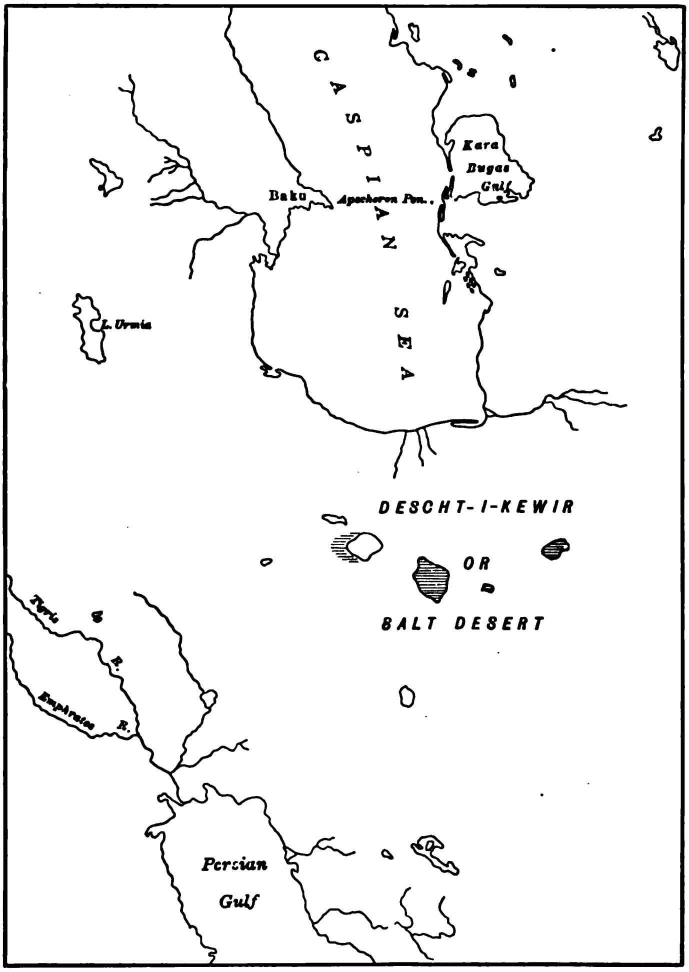

Fig. 67.—Outline map showing the location of the larger salt lakes and plains in the Kewir Desert of Persia.

The great Kavir salt marsh or playa lake is 400 kilometers long and 200 kilometers broad, and is surrounded by loess plains and desert sands. Wadis and gulches extend from the mountains sometimes to its borders, and through them salt and mud is carried to the basin in rainy seasons. Immediately surrounding the lake is a belt of yellow loess and clay, the yellow color being due to the finely disseminated iron hydrate. This material, if buried by other deposits and subject to the dehydration of its iron content, would furnish a deep red, fine-grained formation, comparable to the red beds which are found so intimately associated with the Siluric and other ancient salt deposits of North America and other parts of the world (see Vol. II).

The yellow belt merges outward into a zone of sands upon which steppe grasses grow in luxuriance. Toward the mountains this passes into the zone of coarse clastics, which near the cliffs consist for the most part of angular material.

The playa lake of Kavir is more a lake of liquid mud than one of water. During the dry season it solidifies so that it may be crossed safely along certain routes. The deposit consists in its upper part of a bed of wet clay 10 centimeters in thickness, below which occurs a layer of hard rock salt 7 centimeters thick. Below this, in turn, is a 15 centimeter bed of half dry clay. Below this, the clay is softer and mixed with more water, so that at a depth of 1 meter no bottom could be found on sounding with an iron bar. In places several salt layers were found intercalated between the clay.

The surface of the playa is very uneven, with many swellings and ridges similar to those found by Huntington on the salt surface of the Lop Basin, and by Walther on the salt surface of the salt pan of Mex in Lower Egypt (see *ante*, p. 119). Desert salts of this type, then, will often show a disturbed condition, a feature not uncommonly noted in the salt deposits of older geological periods.

CHARACTERISTICS OF DESERTS IN LARGE CONTINENTS, WHICH AFFECT THE DEPOSITION OF SALTS

Temperature.—Among the phenomena characteristic especially of deserts which lie in the heart of large continents, is the great range of temperature to which the salt waters may be subjected. Thus at Yakutsk in Siberia, latitude 62°N, the annual range of temperature is from +18.8°C. in July (65.8°F.) to −42.8°C. (−45°F.), a range of 61.6° on the Centigrade scale, and of 110.8° on the Fahrenheit scale. This is due to the position of this locality in the heart of the continent, for on the sea coast at the Faroe Islands, in the same latitude, the annual range is only 7.9° on the Centigrade scale, or 14.2° on the Fahrenheit scale. From tropical West Africa, Pechuel-Loesche has recorded summer temperatures ranging from 60° to 84°C. (140° to 183°F.), and similar summer temperatures have been found in other districts. But such temperatures have a more marked influence on salt lakes in the desert than appears at first. As we have already noted, Kaleczinzky[1] in his studies of the Hungarian salt lakes found that while the surface water of the lake, which was essentially fresh, had a temperature of 21°C. (69.8°F.), the brine at a depth of 72 centimeters, which had a salinity of 240 permille, had a temperature of 56°C. (132.8°F.), while elsewhere temperatures of 70°C., or over (158°F.) were recorded for the deeper lying brines of salt lakes.

It is obvious, then, that temperatures high enough for the crystallizing out of most, if not all of the salts of a saline solution, are found in the deserts, though it must be noted that some of the temperatures required for the separation of mother liquor salts are very high. Thus, according to von Bischof,[2] carnallite in solution, loses its water only at a temperature of 120°C. (248°F.) and other temperatures at which mother liquor salts are formed, are equally high. Nevertheless, there is another factor which influences the deposition of these salts, and that is cold.

As we have seen in Chapter III, many of the salts obtained by Usiglio from mother liquor, separated out at night on cooling. Liebig found that carnallite would crystallize out at Salzhausen from a brine, which held it in solution, at winter temperature. Now, winter temperatures in desert regions are far more severe than in north Germany. Przewalski found that at a temperature of − 34°C. (*i.e.*, 29° below zero F.), the salt lake of Tschong Kumkul at an altitude of 3,570 meters above the sea, was still unfrozen, though the temperature of its water was −11°C. (+12°F.,) or about 20°F. below the freezing point. Similar conditions at like low temperatures have been observed by others, and these are not the lowest temperatures found in desert regions.

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[1] Földtani Közlöny, Vol. XXXI, Budapest, 1901.

[2] Die Steinsalzwerke bei Stassfurt, 1864, pp. 27 and

Thus many salts may crystallize out during the period of low winter temperatures, when they would still remain in solution during even the highest summer temperature. (See also salt making on the Siberian coast, Chapter XXXV, Vol. II.)

Influence of Drifting Sands and Dust.—Drifting dust masses, which in deserts often form huge moving clouds, and which even at ordinary times are apt to render the atmosphere hazy, appear to play a rather important part in the preservation of desert salts from re-solutions. The salt surface is strongly hygroscopic, and dust particles drifting over it are apt to be held by the moist, sticky surface. Salt surfaces, after a windstorm, are often found powdered over with dust, presenting an apparently smooth, dry surface, but one which is sedulously avoided by caravans owing to its slipperyness. Such a dust layer, even if only of slight thickness, will preserve the salt from re-solution when new waters accumulate over the surface of the playa.

Wandering sand dunes play an important part in the desiccation of salt lakes. The hot dry sand in passing slowly across the salt surface draws up by capillarity the remaining liquid, which may contain the mother liquor salts, and in this finely divided condition quickly dry out the salts which then become the sport of the winds and are carried away to be deposited elsewhere with the sand or dust. Thus the original salt bed will be freed from its mother liquor salts in so far as these are present, and sodium chloride of great purity will alone remain. Many such salt lakes in the Volga region north of the Caspian have suffered desiccation by drifting sands and the phenomenon is probably a widespread one.

Mother Liquor Salts in Desert Deposits.—From the foregoing it would appear that mother liquor salts are not a characteristic accompaniment of desert salts, though Walther quotes Loczy as finding salts of this type separated out in some of the desert salt seas of Central Asia, probably during the winter months. In the first place, it may be doubted, if the amounts of potash and similar salts are ever as great in the waters rendered saline by connate salts, as is the normal sea water. As we shall see from the analyses of some of the waters of this type, to be given presently, the properties of the various salts differ to a marked degree in at least a number of them. Potash salts are more readily absorbed by the soil than are sodium salts and so will be retained to a greater extent in the desert soils which surround the salt basins. The great fertility of many such soils on irrigation is well known. In the second place, the mother liquor will be absorbed by the drifting sands and so become removed from the salt bed. The mother liquor salts carried away by the wind may be concentrated elsewhere into deposits of these salts which may be preserved by a dust covering of eolian origin. Such deposits of salt will then be unassociated with normal salt beds. It may be doubted, however, that such deposits are ever of great importance. Certainly none have been recorded so far, though the possibility of their existence cannot be questioned. The potash and other salts of the brine of Searles Marsh to be described presently, may possibly have such an origin, though it is more likely that these are derived from the decomposition of the rocks of the desert and are not connate (p. 277).

It would thus seem that a search for potash and other mother liquor salts in older deposits of connate salts is likely to prove unsuccessful, and therefore it is desirable to determine in the first place the origin of a given salt deposit, in order that much expensive search for salts, the presence of which is not indicated by the genesis of the deposit, may be avoided.

Gypsum and Anhydrite in Desert Salt Deposits.—Gypsum has been found associated with desert salt deposits in the form of isolated crystals scattered widely through the sand in which it is formed, but no actual gypsum beds have been recorded as associated with these salts. The smaller gypsum crystals may be gathered up by the wind, and, sorted free from sand, may accumulate as gypsum dunes or layers. It is not difficult to understand this absence of gypsum from the salts of deserts, for the rapidly gathering waters which bring the salt solutions from the surfaces where the salt was formed as an efflorescence, would encounter very little gypsum, and such as they find would not be so readily dissolved as is the ordinary salt. Thus in the first place the water carries little sulphate of lime in solution, and that which it carries is probably all separated out in the passage of the water through the hot sands which surround the salt basin. Thus crystals of gypsum will form in the outer zone of sands and clays, while only pure rock salt and the highly soluble mother liquor salts, in so far as they are present, will be carried to the central basin.

It is possible that when a sufficient amount of calcium sulphate is present in the waters of desert basins that it will be deposited in the form of anhydrite rather than gypsum layers. The conditions of direct separation of anhydrite from solutions carrying calcium sulphate have been studied by Van't Hoff and others,[1] who find that it separates out at a temperature of 66°C., and in the presence of sodium chloride at a temperature of 30°C.

Brauns produced anhydrite by placing a large drop of a saturated solution of sodium chloride or potassium chloride, or a drop consisting of a mixture of both, upon a slide and putting on one side of this a drop of a solution of calcium chloride and on the other one of magnesium sulphate (Bitter salt). Then he allowed both of the outer drops to diffuse through the middle one by making a fine connecting stream, avoiding at the same time the jarring of the slide. The union of the calcium chloride and magnesium sulphate resulted in the formation of calcium sulphate, which crystallized partly as gypsum and partly as anhydrite on slow evaporation, under air, of the liquids, while sodium chloride and potassium chloride crystallized out near the calcium chloride drop in octahedrons or in combination of cubes and octahedrons.

From this he concludes that from a strong solution of sodium chloride the calcium sulphate will separate out as the hemihydrate or the anhydrate (anhydrite) instead of the dihydrate (gypsum). The same holds for the magnesium sulphate which separates as the monohydrate $MgSO_4.H_2O$ (Kieserite) instead of the heptahydrate $MgSO_4.7H_2O$ (Bitter salt or Epsomite), if the solution holds magnesium chloride. Sodium sulphate, which separates from the pure solution under ordinary temperature as the decahydrate ($Na_2SO_4.10H_2O$, Mirabilite) separates in presence of sodium chloride as the anhydrate Na_2SO_4 (Thenardite).

Vater,[2] after a series of experiments, came to the conclusion that at ordinary temperature calcium sulphate would crystallize out as gypsum and not as anhydrite, even from a solution saturated for sodium chloride, and even from solutions carrying

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[1] Van't Hoff and Armstrong, Sitzungsberichte d. Berliner Akad. d. Wiss. 1900, p. 559. Brauns, R. Ueber Nachbildung von Anhydrit. Neues Jahrbuch für Mineralogie, 1894, Bd. 2, pp. 257-264. Van't Hoff and Weigert, Sitzungsbericht, Berl. Akad., 1901, p. 1148.

[2] H. Vater, Einige Versuche über die Bildung des Marinen Anhydrites. Sitzungsberichte der K. Preuss. Akademie der Wissenschaften, Berlin, 1900, pp. 269-294

3 per cent. or more of magnesium chloride. He found further that even from solutions saturated for magnesium chloride gypsum instead of anhydrite would separate at ordinary temperatures. With reference to the experiments of Brauns he concludes that the crystals obtained by that investigator were not anhydrite but a rhombic modification of $CaSO_4$, $2H_2O$, since there is reason to believe that gypsum is dimorphic as has been shown to be the case by Fock for $CaCrO.2H_2O$.

Vater concludes that only with temperatures above 30°C. can calcium sulphate separate as anhydrite, while at the same time calcium carbonate generally separates out as aragonite. Dolomite is formed under similar conditions, and this explains the association of the three minerals in nature.

Van't Hoff and Weigert,[1] on the other hand, find that normal anhydrite forms after some time, from a solution containing calcium and magnesium chloride at ordinary temperature. From their elaborate investigations they reach the conclusion that at 25°C. "Solutions which are saturated for sodium chloride and another salt, show a lower tension than 17.2 with the exception of those which are saturated for sodium chloride and sodium sulphate. (Tension 17.5 mm.) As in this case, the calcium sulphate separates out as part of the glauberite, it follows, that in the mother liquor salt series the formation of gypsum at 25°C. is excluded, and that calcium separates either as double salt or as anhydrite. The special case of seawater is simplified in the same manner, in that in this case, already at the beginning of sodium chloride separation, the tension at 25° has been lowered below 17.2, owing to the presence of chloride and sulphate of magnesium and potassium, and that hence from the beginning of rock salt formation only anhydrite is to be reckoned with, a fact which agrees with the conditions in the anhydrite region [of the Stassfurt Salt]."[2] (See Chapter XXIV.)

As will be more fully shown later, it would appear that under ordinary conditions of evaporation of sea water at low temperatures, gypsum is formed while an excess of chlorides such as would be produced by the addition of connate salt to an evaporating basin results in the separation of anhydrite. Anhydrite and dolomite form under similar conditions of temperature and pressure. The Rauchwacke, a porous dolomite of the Zechstein, was originally a mixture of dolomite and anhydrite, the solution of the latter having left the characteristic pores.[1]

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[1] Van't Hoff, J. H., and Weigert, F., Der natürliche. Anhydrit und dessen Auftreten bei 25°. Sitzb. K. Pr. Akad. d. Wiss., Berlin, 1901, pp. 1141–1148.

[2] *Loc. cit.*, p. 1148.

Gypsum may, however, be formed by the subsequent alteration of beds of limestone, as has been frequently observed in limestone regions and will be more fully discussed in the chapter on the meta salts. Since beds of limestone may readily be associated with salt in desert regions, the association of secondary gypsum with salt is to be expected. This is shown to be the case in the Siluric salt deposits of New York, as will be more fully discussed in a future chapter.

Limestone Deposits in Association with Desert Salt Beds.—The deposition of calcium carbonate obtained by solution from limestones in the hills which surround the desert, and the evaporation of the water on the desert floor, is a well-known phenomenon and will be more fully discussed in the next chapter. That under certain conditions such layers of calcium carbonate may be deposited over a salt bed, or may be succeeded by a deposit of salt, cannot be questioned. Even deposits of dolomite may be formed in this way, but it must be said that observations along this line are very imperfect. It should here be noted, however, that the calcium carbonate which is carried into the standing salt water of Great Salt Lake by its affluents is all precipitated near the mouths of these streams, but here we deal with a salt lake rather than a playa (see beyond). At present no good example of a playa carrying connate salts and calcium carbonate layers is known.

A very different source of lime carbonate may, however, be postulated for desert salt basins situated entirely within limestone regions, as was the case with some of the salt deposits of the ancient New York desert (Salina, see chapter XXII). Where the prevailing rock of the desert rim is a limestone, this by disintegration will not only furnish the connate salts enclosed in it, but will produce lime sand and dust such as is little known in regions of pluvial climates where destruction of limestone goes on largely by solution. It is scarcely to be doubted that in arid climates limestone will disintegrate under the influence of alternate heat and cold, especially if the limestone is of a semi-crystalline or crystalline character. Examples of such disintegration of crystalline limestones and dolomites are well known, even in pluvial climates such as that of the vicinity of New York City, where the Inwood limestone of New York and of Westchester County furnishes a good case in point. Unfortunately our knowledge of the extent of disintegration of limestones in desert regions is very meagre, observers having paid little attention to this matter. That it takes place, however, cannot be denied, and the fact that many of the crescentic dunes or barchanes of Turkestan are largely composed of lime sand proves its importance. If, then, the prevailing material for eolian transport is lime-sand and dust, desert salt lakes may at intervals be overwhelmed by such deposits, as they are known to be by quartz sands and siliceous dusts. In this manner a regular interstratification of salt and lime-dust deposits (calcilutytes) may be formed, an interstratification eminently characteristic of some older salt deposits of desert origin, where the postulated conditions for such depositions are known to have prevailed.

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[1] W. Frantzen, Jahrb. d. König. Preuss. Landesanstalt und Bergakad., 1894, p. 65.

As already noted and as will be more fully described later, such limestones may be altered to gypsum by secondary processes, and it is not impossible that a further alteration may produce anhydrite, though such a final change has not yet been observed.

SECONDARY DEVELOPMENT OF SALT DEPOSITS ON THE FLOOR OF A SHRINKING SALT LAKE

When a large body of salt water, such as a cut-off from the sea, shrinks by evaporation, its main salt deposits will be concentrated in the lower depressions of the basin floor, where a normal succession of gypsum (or anhydrite), rock salt, and under favorable conditions mother liquor salts, will be formed. On the flat floors of the basins around these deeper portions, which are progressively exposed with the shrinking of the water in the main basin, secondary salt accumulations will, however, form, which have their distinctive character. These should be expected in the marginal areas of all salt deposits formed by evaporation of a cut-off.

The Caspian Sea has already been described as a water body formerly of much greater extent, which has been reduced by evaporation until its surface now lies 84 feet below the level of the sea and more than a hundred feet below some of the still recognizable older shorelines which are found around its borders. Over vast areas on the north and northeast in the government of Uralsk in Asiatic Russia, and on the west in the governments of Stavropol and Astrakhan, extend the plains which formerly were a part of the Caspian floor and have become uncovered as the result of the shrinking of this lake. Here are found more than 2,500 salt lakes and playas, their number constantly increasing as the retreat of the Caspian water goes on.

Over the dry surface of these wide plains the salt which was left by the waters which once covered it and much of which, as connate salt, occupied the sand and mud deposits formed on the bottom of that lake, now appears as efflorescences on the surface, forming fine crystals which cover the surface like a layer of newly fallen snow. In every depression are salt pools which dry up during the hotter season and become covered as with a layer of ice. The larger lakes receive as affluents, during the moister period, streams which have dissolved the salt from the sand and soil through which they flow, or in some cases are fed by brine springs derived from the older salt deposits of the region (Permic, etc.).

With the beginning of the hot dry season, the water of these lakes becomes condensed owing to the strong evaporation from its surface. Salt begins to separate out, especially with the lowering of the temperature in the evening, and continues during the night. It forms as more or less regular cubical crystals which unite into a crust over the surface of the water, and which, with increasing size and when the crust is broken by the wind, sink to the bottom or are drifted to the shore where they accumulate as a snowy sheet, much as ice does in our lakes in winter. Beds of salt of varying thickness are formed on the floor of the lake, especially in the center where the lake is deepest, the thickness being dependent on the degrees of concentration of the water, its temperature, and the character of the climate. The precipitated salts formed during one season constitute a loose granular aggregate which consists of sodium chloride and bitter salts. These, when exposed to the air, quickly deliquesce. In the course of the winter this new salt, as it is called, unites more and more into a solid mass, from which in the spring the rain and melting snow waters leach out the more soluble magnesium and other salts, leaving the sodium chloride, which unites into a solid mass of pure rock salt. This is then known as the "old salt" which alone is the object of exploitation.

During the wet period the streams often carry much mud which is deposited in the lake over the salt, as a layer of black, ill-smelling material known as "batkak." These layers vary in thickness from 11 millimeters to 53 centimeters. Such mud, as well as sand layers form a constant alternation with the salt deposits and thus represent a parallel to the annual rings of anhydrite in the pure evaporation products of some older salts, as will be described in a future chapter.

On the bottom of the lake, below the lowest pure salt beds, these layers of "batkak" alternate to unknown depths with layers of sulphate salts, especially sodium sulphate, magnesium sulphate, some sodium chloride and magnesium chloride, the whole mixed with mud and of a gray or bluish color. Downward these layers increase in firmness and become progressively darker. Sometimes in summer the lakes dry out completely, leaving a crust of salt, but more generally a layer of brine remains, varying in depth from about 1 meter in spring, to a third that amount in mid-summer. Analyses of the brine (rapa) of two such lakes gave the following composition.

TABLE XXVIII.—ANALYSIS OF BRINE (RAPA) FROM PLAYA LAKES ON CASPIAN PLAINS

	In 100 parts of brine by weight	
$NaCl$	10.5387	13.9997
$MgCl_2$	9.9124	5.4349
$MgSO_4$	8.2201	
$CaSO_4$	....	0.0280
KCl	....	0.1992
$MgBr_2$	....	0.0065
Water	71.3288	70.3317
Total	100.0000	100.0000
Salinity permille	286.7120	296.6830

In summer the salt on the bottom of the shallow lakes is broken up by bars or shovels, the mud scraped off from the underside, and the broken fragments washed in the brine, after which they are shoveled into shallow boats. These are generally dragged by the wading workmen to the shore or to specially prepared platforms where they are piled up and left to dry. Salt thus obtained is hence called "drag salt" (Germ. Schleppsalz). In 50 days, 750 men will gather 6 million pud (96,280 metric tons). Piled into pyramidal heaps, the salt is left to age for 2 years before it is placed in the market. (See further description of Elton and Baskuntschak lakes in Astrakhan, pp. 200–203.)

SALT LAKES LARGELY IMPREGNATED WITH CONNATE SALTS

The Great Salt Lake of Utah.—This lies in the deepest portion of the basin of a former great fresh water lake, Lake Bonneville, the shorelines of which are still traceable around the margin of the old basin (Fig. 68). The lake is not a remnant of a former cut-off portion of the sea, as has sometimes been supposed, for the Tertiary deposits which surround and underlie it are of continental origin. The lake is similar to that of the Lop plain, lying within a tectonic basin, but unlike that basin the West American one was formerly filled by fresh water, and the present water body is a lake, not a playa.

The salt is probably connate in origin, derived from the older marine limestones and other rocks which have been exposed by uplift and erosion in the neighboring mountains. Some of this salt may, of course, have been deposited in the older continental sediments of the region (Permic to Tertiary), and is now merely redeposited. Meta-salts and volcanic salts appear to be absent from this basin, though the former may be developed to some extent in the neighborhood. The immediate source of supply seems to be the soil of the surrounding desert basin in which the salt finds a temporary resting place on its passage from the rocks in which it existed in the connate state, to the lake basin where it finds its last resting place for the time being.

The following table shows the analyses of the water of this lake collected from 1869 to 1913, and brings out especially the variation in salinity,[1] which shows an almost steady increase to a maximum in 1904, after which a decrease set in. Ocean water is given for comparison.

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[1] Clarke, "Data of Geochemistry," 3d ed., p. 155.

TABLE XXIX.—ANALYSES OF SALTS IN SOLUTION OF THE WATER OF GREAT SALT LAKE DURING AN INTERVAL COVERING NEARLY 50 YEARS

	Ocean water	Waters of Great Salt Lake							
		1869	1877	1879	1889	1892	1904	1907	1913
Cl	55.292	55.99	56.21	55.57	56.54	55.69	55.25	55.11	55.48
Br	0.188	Trace	......	......	......	Trace	Trace		
SO_4	7.692	6.57	6.89	6.86	5.97	6.52	6.73	6.66	6.68
Co_3	0.207	......	0.07	......	......	......	......	......	0.09
Li	....	Trace	......	......	......	0.01	Trace		
Na	30.593	33.15	33.45	33.17	33.39	32.92	34.65	32.97	33.17
K	1.106	1.60	?	1.59	1.08	1.70	2.64	3.13	1.66
Ca	1.197	0.17	0.20	0.21	0.42	1.05	0.16	0.17	0.16
Mg	3.725	2.52	3.18	2.60	2.60	2.10	0.57	1.96	2.76
SiO_2	......	......	......	......	......	0.01			
Fe_2O_3 Al_2O_3	......	......	......	......	......				
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille	35.00	149.94	137.90	156.71	195.58	230.355	277.2	229.9	203.49

TABLE XXX.—ANALYSES OF THE SALTS IN THE WATERS OF STREAMS TRIBUTARY TO GREAT SALT LAKE

	Bear River, Evanston, Wyo.	Bear River, Utah, near its mouth	Jordan River intake, Utah and Salt Lake Canal	Jordan River near Salt Lake City	City Creek, Utah	Ogden River, Ogden, Utah	Weber River, mouth of canyon
Cl	2.68	32.36	35.54	34.76	5.38	23.21	13.73
Br	....	......	....	....	......	......	......
SO_4	5.76	8.16	26.54	30.68	2.87	5.65	9.25
CO_3	52.68	21.53	2.67	Trace	52.57	33.68	40.00
Li							
Na	4.49	20.54	26.13	23.04	3.74	11.31	8.37
K						4.16	4.19
Ca	23.69	10.12	7.59	10.26	24.19	16.05	18.19
Mg	6.86	4.76	1.53	1.26	7.15	5.94	6.27
SiO_2	3.84	......	....	....	3.69		
Fe_2O_3 Al_2O_3	....	2.53	....	....	0.41		
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity permille	0.185	0.637	0.892	1.000	0.243	0.444	0.455

Comparison of Analyses.—A comparison of the waters of Great Salt Lake with those of the ocean shows a rather marked similarity except that the carbonate and the lime have nearly all been precipitated out, the latter probably in the form of gypsum, although the salinity was hardly high enough for that (202 permille) in the earlier years. It is, of course, apparent that saline bodies of water produced by the concentration of connate ocean waters are apt to have a different composition from that of the

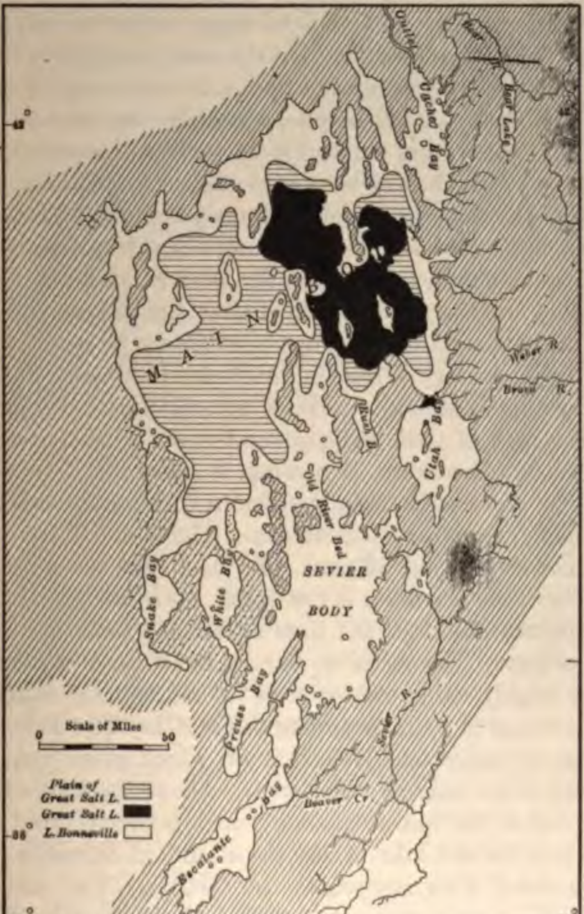

FIG. 68.—Map of Lake Bonneville. (*Redrawn after Gilbert.*)

sea, since differential solution of the liberated salts is more likely to occur than not. The wonder is that the waters of Great Salt Lake correspond so closely in composition to those of the ocean. The large amount of potassium is probably also unusual for such waters, since clays are able to take up considerable proportions of potassium and to remove its salt from solution (Clarke, p. 138). Thus the potassium of natural waters tributary to such salt basins is removed, as these waters percolate through the soil, or else is taken up by suspended silt carried by the streams. Sodium is removed in this manner to a much less degree, and hence concentrated connate salts will be high in this metal; but, on the whole, poor in potassium. On the other hand, this tendency serves to increase the amount of potassium taken up by the finer portions of the oceanic sediments, especially the clays so that in cases of connate waters derived from such sediments there is a counterbalance which may be of importance. Analyses of ocean sediments bearing on this point are largely lacking, and we cannot at present state whether connate waters of calcareous sediments do or do not enclose more than the normal amount of potash contained in ordinary sea water. That the deep sea red clay does contain such an excess, is, however, shown by recent analyses made in the laboratory of the United States Geological Survey.[1]

When we compare the waters of the tributaries of Great Salt Lake with those of that body, several noteworthy facts appear. Bear River, at Evanston, Wyoming, is a normal river water of low salinity, and carries mainly calcium carbonate, which would be the chief deposit on evaporation. The same is true of City Creek, another normal affluent. By the time Bear River has reached the lake, however, it has taken up a considerable quantity of sodium chloride, the lime carbonate therefore being in less proportion. The salinity, too, is more than tripled. The Jordan, a highly saline water rises in the equally saline Utah Lake, and brings in a similar amount of NaCl. To a lesser degree this is true of Ogden and Weber rivers, which come from the region of the older marine sediments. All of these streams are, however, rich in calcium carbonate, which is precipitated on their entrance into the salt lake, where the abundant chlorides produce supersaturation with respect to the $CaCO_3$. The oolitic lime sands which abound at various points along the lake shore are probably in part, at least, the results of such precipitation, though Rothpletz holds that these are formed by the physiological activities of minute algæ, as well as by the peculiar crustacean fauna of this lake. Among the interesting deposits formed from the waters of Great Salt Lake, is sodium sulphate in the form of the decahydrate mirabilite ($Na_2SO_4.10H_2O$). This, however, is formed only in winter, when it is cast up in heaps upon the shore. In warm and dry air, mirabilite loses its water and is changed to the anhydrous sulphate thenardite. Sodium chloride is formed as incrustations in marginal pools upon drying.

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[1] Clarke, "Data of Geochemistry," 3d ed., p. 139.

Salt has been obtained from the waters of Great Salt Lake since 1848, when the Mormons began collecting it along the shores of the lake from the pools, which on evaporation of the water in the dry season are covered with a crust of salt. Solar evaporation of the water in artificial pans began about 1860. In 1906 the production was 36,710 short tons.

Sevier Lake, Utah.[1]—This lake like Great Salt Lake is a concentration of connate waters. It is at times entirely dry, depositing a crust consisting in part of sodium chloride and in part of sodium sulphate. In 1872, when the waters had a salinity of only 86.400 permille, the composition was as follows:

TABLE XXXI.—ANALYSIS OF SALTS IN WATERS OF SEVIER LAKE

Cl	52.66
SO_4	10.88
Na	33.33
Ca	0.12
Mg	3.01
	100.00

Chlorides and sulphates alone were present, carbonates being entirely absent and lime almost so. On drying, the water deposits sodium sulphate, which is especially abundant near the center, while around the margins sodium chloride is the chief evaporate. The following analyses show these deposits.

TABLE XXXII.—ANALYSES OF SALTS DEPOSITED BY SEVIER LAKE

	Margin	Center
Na_2SO_4	14.3	84.6
Na_2CO_3	.....	0.4
NaCl	75.8	7.0
$CaSO_4$	.....	Trace
$MgSO_4$	5.5	Trace
K_2SO_4	0.7	
H_2O	3.6	8.0
Insoluble	0.1	Trace
	100.0	100.0

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[1] G. K. Gilbert, Mon. U.S.G.S., Vol. 1, 1890, pp. 224-227.

As is brought out both by the analysis of the brine and that of the salts, potassium is practically absent, a feature which appears to be significant for deposits formed by the concentration of connate salts.

It may here be again remarked that even if normal bitterns should be formed over the surface of such a drying lake, the chances for the preservation of such salts are slight. As we have seen, salt beds deposited from lakes of this type and still covered by a thin sheet of bittern, when overwhelmed by desert sands will have these bitterns absorbed by the sand and forced to rise by capillary attraction to the surface. Here the efflorescing salts will be scattered in the dust by winds, and come to be lost completely. Thus only pure beds of rock salt, free from mother liquor salts, will remain; and this is probably normal for deposits of this type which are always situated in deserts.

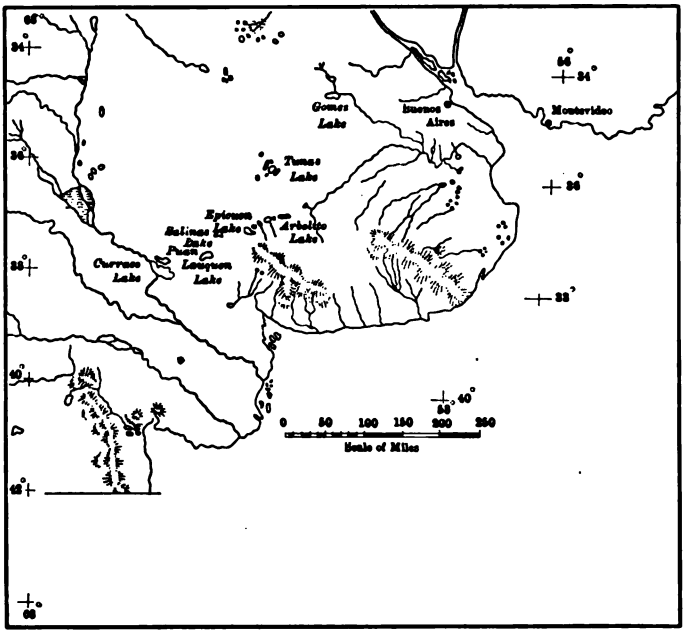

FIG. 69.—Outline map of the region around Buenos Aires, showing the location of saline lakes.

Salt Lakes or Lagunas of Chile and Argentine, South America.—On the arid plateaus and pampas and in the inter-montane valleys of Chile and the Argentine, occur many salt lakes or playas, some of which contain nearly pure rock-salt deposits, while others are rich in nitrates, borates and other salts. These latter will be discussed in a subsequent chapter. Here we may cite as examples of salt lakes [illegible] [illegible] in sodium chloride the Laguna of Tarapaca in Chile and the Laguna de Epecuen in Argentina. The similarity of the waters of these lakes to seawater is rather striking, though the low percentage of [illegible] of the lime and magnesia is significant. These salts apparently derive their

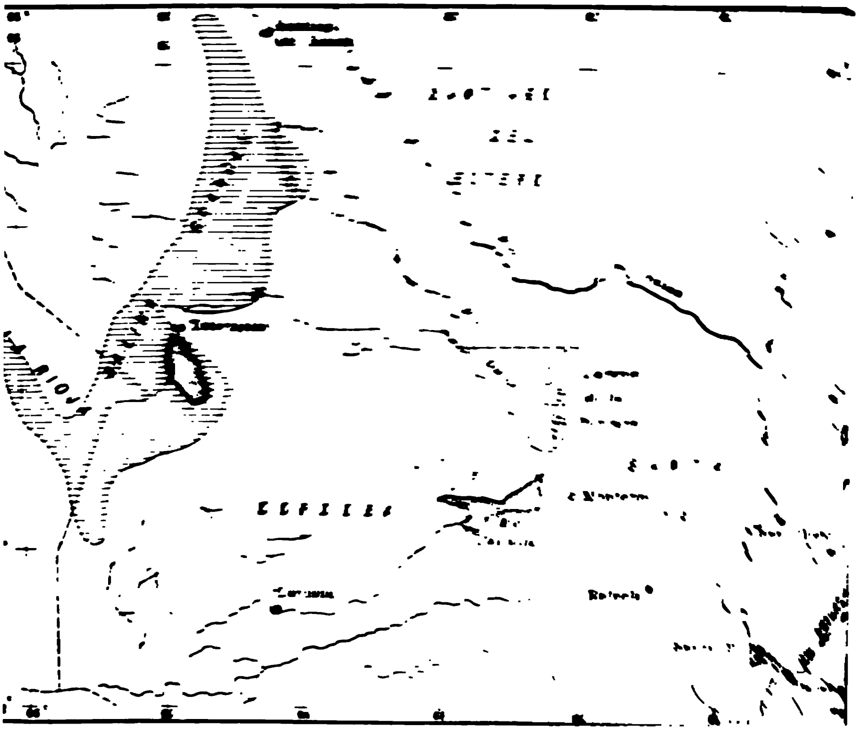

Fig. 70.—Outline map of a part of Northwest Argentina [illegible] of Salina Grandes, the R. Salado, Laguna [illegible]

salts from solution of older salt beds, though some of it may be from connate sources. The Laguna de Epecuen is one of a number of small lakes of the Argentinian pampas, lying in the western part of the province of Buenos Aires at about latitude 37°S, and therefore in the region of the southwesterlies, which are intercepted by the High Cordilleras and so produce a certain amount of aridity during a part of the year (Fig. 69).

In the following table the analyses of the lake waters are given, together with that of the Rio Saladillo, which flows into the Laguna de los Porongos in northeast Cordoba, Argentine (Fig. 70). This river has a high salinity during the dry season, but is nearly fresh in the rainy season. According to the estimates of Stelzner[1] it carries 584,566,200 kilograms of salts into the lagoon every year. Practically all of this salt is originally derived from the solution of older salt beds, though the immediate source is apparently the Salina Grandes from which this river receives affluents.

TABLE XXXIII.—ANALYSES OF LAGOON WATERS OF CHILE AND ARGENTINA[2]

	Ocean water for comparison	Lagoon of Tamentica, Chile	Laguna de Epecuén, Argentine	Rio Saladillo, Argentina, at Puente del Monte
Cl	55.292	50.44	42.96	56.74
Br	0.188			
SO_4	7.692	9.17	17.19	4.82
CO_3	0.207	......	2.13	
NO_3	....	2.14		
Na	30.593	35.35	37.72	36.40
K	1.106	2.29		
Ca	1.197	0.01	......	1.63
Mg	3.725	0.60	......	0.41
	100.00	100.00	100.00	100.00
Salinity in permille	35.00	285.50	285.00	108.25

Desert Lakes of Australia and Africa.—Australia lies between 10 and 40 degrees south latitude and is therefore mostly within the belt of the southern trades. The entire eastern coast is flanked by mountains, some of which often rise to great altitudes. The interior of Australia is a vast desert area, still in large part unexplored and dotted with numerous saline lakes and salinas, of which Lake Eyre and Lake Amadeus are the largest (Fig. 71). Lake Torrens is perhaps the best known of these, and it and Lake Fowler have produced considerable salt. Into these lakes the intermittent drainage from the eastern ranges as well as from local mountains is carried, and there evaporates, depositing its

[1] Beiträge zur Geol. u. Pal. der Argentinischen Republik, 1885.

[2] See further Chapter XXXVII, Vol. II.

load of salts carried in solution as well as the clastic material carried in suspension and rolled along. The Cooper River, one arm of which enters Lake Eyre, has built a delta or alluvial fan of vast extent, its length being nearly 185 miles and its width over 170 miles, while its area is more than twice that of the Nile Delta. This clastic deposit merges laterally into the salts separated out from the lake.

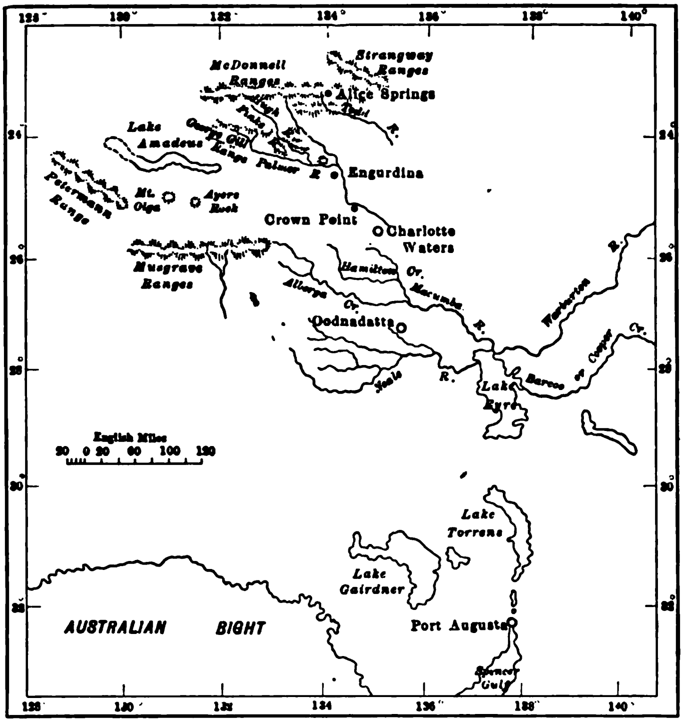

FIG. 71.—Outline map of the lake district of Central Australia. (*Redrawn after Spencer and Gillen Across Australia.*)

The salt of these inland lakes is entirely of connate origin being derived from the leaching of the connate salts of the older marine sediments. It is true there are a few small local salt beds in New South Wales, but these probably furnish supplies of salt for a few streams only.

Most of the lakes contain bitter salts, as well as sodium chloride, but some of them are almost pure solutions of common salt. This is shown by the analysis in column 1 of the following table, which represents the salts in the water of Lake Corongamite,[1] a small lake in Victoria, with a salinity of 46.039 permille (see further, Chapter XXXV, Vol. II).

In the second column is given the analysis of the salts from the waters of a salt lake 32 kilometers north of Pretoria in the Transvaal (about 25°+ S latitude). This lake or salina is about 400 meters in diameter and occupies a funnel-shaped depression in granite. Its salts are probably wholly of connate origin, and it has a salinity of 211.4 permille.[2]

TABLE XXXIV.—ANALYSES OF SALTS FROM THE WATERS OF AUSTRALIAN AND SOUTH AFRICAN SALT LAKES

	A	*B*
	Lake Corongamite, Victoria, Australia	Salt Lake, 32 km. north of Pretoria, S. Africa
Cl	59.32	43.47
Br	0.22	
SO_4	1.65	0.03
CO_3	Undet.	15.17
Na	35.07	41.33
K	0.84	
Ca	0.13	
Mg	2.77	
Total	100.00	100.00
Salinity permille	46.039	211.40

THE SALT VLEYS OF SOUTH AFRICA

Under this name are included a series of shallow excavations or erosion hollows in the surface of the desert lands or velts of South Africa, especially in the Kalahari desert, in which salt frequently accumulates through leaching from the surrounding soil and evaporation of the water under the influence of the hot sun and winds. They are also called salt-pans, but as we shall restrict this name to the coastal pans, the local name salt vleys will be adopted for this inland type. Passarge has described these in great detail in his book "Die Kalaharie." They cover the entire South African upland, and comprise several types among which the following are the chief ones:

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[1] A. W. Craig and N. T. M. Wilsmore, Fourth Rept. Australasian Assoc. Adv. Sci., 1892, p. 270.

[2] E. Cohen, Min. pet. Mitt., Vol. 15, 1895, pp. 1, 194.

1. *Simple Sand Vleys.*—Flat shallow hollows with a floor of humus, lying in the sand of the steppe, especially in the old river beds and depressions. No rock bottom or rim.

2. *Rock Bottomed Sand Vleys.*—Flat funnel-shaped depression with a floor of solid rock or salt marl, covered by sand.

3. *Brack Vleys.*—Round or oval hollows in soft tuffaceous and mostly saliferous limestone, often several kilometers in diameter. Covered with salt efflorescences, and forming salt licks (bracken) for the herds of the velts.

4. *Salt Vleys.*—Similar to the preceding, but larger. They form in drainless areas and in them are deposited sodium sulphate, sodium carbonate, gypsum and especially salt marl, which is a mixture of lime-mud, some clay and more or less sand and salt, of various kinds.

5. *Lime Tufa Vleys.*—Hollows in which a soft calcareous tufa is deposited.

6. *Rock Kettles.*—Hollows in the country rock.

In the rainy season many of these hollows are filled with salt water from the leaching of the salt in the material which forms the floor or walls of the hollow. Some of these vleys overlie older salt beds, by the solution of which their water is impregnated. When dry, the surface of these vleys is often covered by an efflorescence of salt. Salt, however, does not occur in all of these vleys. Many if not most of these hollows which form the vleys are due according to Passarge to zoogenic erosion, *i.e.*, they are formed by the herds of animals which in thousands lick the salt efflorescence of the surface ("braken"—Burish) or drink where original inequalities in the surface permitted the accumulation of standing water. These animals trample the rock or soil surface into powder which is then swept away by the wind. When water begins to accumulate in quantity, animals further resort to these places to bathe and wallow. Rhinoceroces, buffaloes, elephants, wild boars, etc. wallow and roll in the mud, and carry some of it away on their hides. Thus the hollows are gradually deepened, and shallow pools are formed filled either with salt, brackish or fresh water according to the nature of the soil. Several of these salt lakes will be described in the discussion of the South African salt deposits (Chapter XXXV).

CHAPTER X

SALTS LEACHED FROM OLDER ROCK-SALT DEPOSITS

That the brines of many modern salt lakes and salt deposits as well, are secondarily derived from the leaching of older salt beds, is a well known fact. Such salt lakes may exist even in moderately pluvial climates, though the redeposition of the salt would only take place where sufficient aridity exists. Of these leached salts the chlorides are perhaps the most significant, though sulphates and carbonates are equally subject to such solutions. Indeed, in the less saline lake and river waters the carbonates as a rule predominate, owing to the familiar fact that carbonate rocks, especially carbonate of lime, form a much larger portion of the earth's crust than do chlorides or sulphates. Carbonate of lime deposits of this type, however, are of little economic value.

CHLORIDE SALTS DUE TO SOLUTION OF OLDER ROCK-SALT DEPOSITS

Among the many modern saline lakes and playas of the earth's surface there is a considerable number whose salinity is due to their being situated in the proximity of older salt beds by the leaching of which their waters are supplied with common salt. Perhaps the best known, though not the most perfect example of such a water body is the Dead Sea of Palestine, which, moreover, is situated in a region of moderate aridity.

The Dead Sea (Fig. 72).—This water body (about 40 miles long by about 8 miles wide) lies within a great fault valley of recent geologic date (Pleistocenic) which finds its southern continuation in the Gulf of Akabah, the eastern horn of the Red Sea, and its northern one in the valley of the Jordan and the Sea of Galilee. The level of the Dead Sea is 1,292 feet below that of the Mediterranean,[1] which is only 50 miles away; while the level of the Sea of Galilee stands at 682 feet below that of the ocean. The distance between the two lakes is about 65 miles, the fall of the Jordan River which connects them being thus, except for its meanderings, a little under 9½ feet per mile. The sides of the rift valley rise steeply, so that for the most part the area below sea level is very narrow.

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[1] In 1848 Lieut. Lynch of the U. S. Navy ran a line of levels and determined the level of the Dead Sea to be 1316.7 feet below that of the Mediterranean.

In the fault scarps which face the lake, older beds of rock salt are exposed. The most noted of these is in a hill known as Djebel-Usdum and is situated on the southwestern corner of the lake. This hill, which is about four miles long and less than a mile wide, consists at the base of a bed of rock salt 50 to 60 feet thick, overlain by red and green clays with gypsum crystals, the whole being covered by white chalky limestone which has been considered of Cretacic age, but according to Blankenhorn[1] belongs to the Quaternary. The exposed salt has been carved by the weather into columns and pillars often of peculiar shape among which is the frequently renewed statue of Lot's wife. Other salt deposits are exposed along the borders of the Dead Sea and elsewhere in this region.

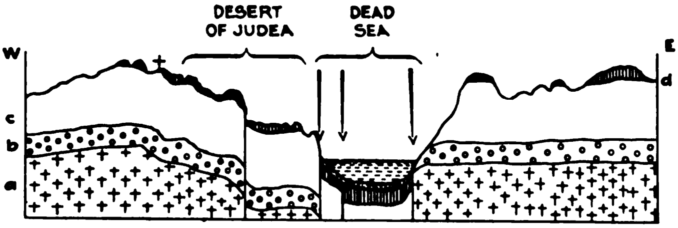

FIG. 72.—Cross-section of the Dead Sea. *a.* Permo-carbonic and crystalline formations. *b.* Nubian sandstone: Cenomanian. *c.* Cretacic limestones, marls and dolomites (Cenomanian, Turonian and Santonian). *d.* Campanian or middle Senonian with phosphates and asphaltic limestones. Below the waters of the Dead Sea are Quaternary deposits. The arrows indicate the position of the faults of the Dead Sea Graben. (*After Blankenhorn.*)

The salinity of the waters of the Jordan River, the chief affluent of the Dead Sea, is 1.61 permille, though rising near Jericho to 7.7 permille. That of the Dead Sea ranges normally from 192.153 at the surface, to 259.980 at 300 meters below the surface. In the following table a series of analyses of the waters of the Dead Sea by Terreil are given, together with one of the waters of the Jordan near Jericho by R. Sachsse.

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[1] Zeitschrift für Praktische Geologie, Vol. 5, p. 360.

TABLE XXXV.—ANALYSES OF THE SALTS IN WATERS FROM DEAD SEA AND RIVER JORDAN (CLARKE, BULL. 616, P. 167)

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
Cl......	65.81	70.25	68.16	67.66	67.84	67.30	41.47	55.292
Br.....	2.37	1.55	1.99	1.98	1.75	2.72	......	0.188
SO_4....	0.31	0.21	0.22	0.22	0.22	0.24	7.22	7.692
CO_3....	Trace	Trace	Trace	Trace	Trace	Trace	13.11	0.207
NO_3....	......	......	......	......	......	......	Trace	
Na.....	11.65	6.33	10.21	10.20	10.00	5.50	18.11	30.593
K......	1.85	1.70	1.00	1.62	1.79	1.68	1.14	1.106
Ca.....	4.73	5.54	1.53	1.51	1.68	6.64	10.67	1.197
Mg.....	13.28	14.42	16.89	16.81	16.72	15.92	4.88	3.725
SiO_2....	Trace	Trace	Trace	Trace	Trace	Trace	1.95	
$AlFe_2O_3$	......	......	......	......	......	......	1.45	
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille..	192.15	207.09	242.63	245.73	251.10	259.98	7.70	35.00

A. Surface water, north end of lake.
B. At depth of 20 meters, 5 miles east of Wady Mrabba.
C. At depth of 42 meters near Ras Mersed.
D. At depth of 120 meters, 5 miles east of Ras Feschkah.
E. Same locality as *D*, at depth of 200 meters.
F. Same locality as *B*, at depth of 300 meters.
G. Jordan River water near Jericho (Sachsse).
H. Ocean water for comparison.

An examination of this table shows several striking characteristics. While chlorine is high, sodium is present to only about one-third the amount found in ocean water. The amount of calcium varies at different points and depths, but the magnesium content is fairly constant and very high, from 4 to 5 times that of ocean water. Other characteristic features are the high percentage of bromine and the small content of sulphates. As Clarke remarks, the brine resembles to some extent the mother liquor left by ocean water after extraction of salt. Still there are very important differences which show that this water cannot be regarded wholly as residual sea water.

A comparison of the water of the River Jordan with that of the Dead Sea brings out some striking differences. The most marked is perhaps the high percentage of sulphates and carbonates of the Jordan water, (on the average about 0.52 permille of the former and 0.32 permille of the latter) and the excess of sodium chloride over the magnesium chloride. As the Jordan water enters the Dead Sea, its carbonates and sulphates (gypsum) are precipitated, so that its contribution to the salinity of the Dead Sea is almost entirely in the form of chlorides. The carbonate and sulphate of lime, as well as the sodium chloride of the river water, are derived from the solution of the country rock. It is clear that there are other sources than the Jordan from which the mineral matter of the water is supplied. The numerous short, temporary streams which descend the steep declivities bordering the lake aid in bringing material in solution from local sources, chiefly the salt beds before mentioned. Hot Springs likewise contribute to the salinity of the water, probably furnishing the bromine.

The great depth of the Dead Sea (1,300 + feet) prevents ascertaining whether or not precipitates are found on its floor; but it is quite probable that such occur.

In the following table two analyses are given in the form of salts, which serve to emphasize the peculiarity of these waters. Ocean salts are again given for comparison. The quantities are given in permillages, or grams per liter.

The larger figures given in the last column indicate the amount of the salt present if ocean water were increased to the density of the water in the second column. This shows that in the largest analysis sodium chloride is about two-thirds the amount found in the ocean.

As has been stated above, the carbonates and sulphates of lime of the Jordan water are precipitated on entering the lake at its northern end; and it is not impossible that deposits of chlorides occur on some parts of the floor of this water body, since as we may see from Table XXXV, the salinity of the water regularly increases downward and may in some sections reach a sufficient height for the separation of such salts. In any case, it is easy to understand that increasing aridity, or a diversion of the Jordan waters, would lead to a stage where salts would separate, and this might continue until extensive deposits are formed. Indeed, if the supply of salt were sufficient, beds of salt of various kinds might accumulate to a considerable thickness in the course of time. Such salts would differ, of course, from the normal sea-salts, although sodium chloride would

TABLE XXXVI.—SALTS IN DEAD SEA AND IN OCEAN IN GRAMS PER LITER

	Dead Sea according to		Ocean water, gr. per l.
	Fürer, gr. per l.	Ramsay, gr. per l.	
1. Sodium chloride (NaCl)........	62.438	121.10	27.213 187.43
2. Magnesium chloride ($MgCl_2$)...	108.015	78.82	3.807 26.220
3. Calcium chloride ($CaCl_2$)......	29.811	24.45	
4. Potassium chloride (KCl)......	14.250	12.17	
5. Calcium sulphate ($CaSO_4$).....	1.021	......	1.260 8.678
6. Magnesium sulphate ($MgSO_4$)..	....	......	1.658 11.419
7. Potassium sulphate (K_2SO_4) ...	....	......	0.863 5.943
8. Sodium bromide (NaBr).......	4.236		0.076 0.5284
9. Magnesium bromide ($MgBr_2$)...	....	......	
10. Calcium carbonate ($CaCO_3$)....	....	......	0.123 0.8471
11. All other salts................	......	4.52	
	219.771	241.06	35.00 241.06

even here play an important part. Magnesium chlorides too would form from waters of this type, and bromides would form an unusual element of the salt series. Finally, potassium salts of not inconsiderable extent might result from the final desiccation of such a water body.

The important fact to be kept in mind here is that differential solutions of older salts, probably of marine origin, complicated by various additions from other sources, produces a solution in which elements, normally rare in, or absent from, marine waters, may occur in considerable quantities and that therefore such salts might be precipitated in much larger quantities than is the case in ocean waters. The importance of this, in the study of older salt deposits should not be overlooked.

Finally, it should be emphasized that such deposits will be entirely free from organic remains except that certain river types may become enclosed in the sediments and precipitates, which form near the debouchures of the feeding streams. Thus, near the mouth of the Jordan, a few river fish are found; but these are quickly killed in the denser portions of the waters, and their remains, when not destroyed by complete decay, are entombed in the chemical as well as the clastic deposits of that portion of the lake.

Other Examples of Saline Lakes Deriving Their Salt from Re-solution

In the following table is given an analysis of a saline lake in Hungary and of two in Russia which derive their salt from the re-solution of older deposits.

TABLE XXXVII.—ANALYSES OF SALTS IN THE WATERS OF ILLYES LAKE, HUNGARY, AND ILETSK AND ELTON LAKES, RUSSIA

Ions as recalculated by Clarke	Illyes Lake	Iletsk Lake	Elton Lake
Cl	60.18	60.26	64.22
Br	Trace	Trace	
SO_4	0.44	0.47	6.82
CO_3	0.04	......	0.04
Na	39.02	38.86	11.27
K	....	Trace	
Ca	0.25	0.33	0.19
Mg	0.03	0.08	17.55
Fe_2O_3	Trace		
SiO_4	0.04		
Total	100.00	100.00	100.00
Salinity in permille	233.747	155.23	265.00

Illyes or Medve Lake, Hungary.—This lake, near Szov̌ata, Hungary, is another example of a water body the salinity of which is due wholly to the solution of older salt deposits. The same thing is true of the neighboring Black Lake. These lakes were formed by recent subsidence and are essentially strong solutions of sodium chloride formed by the leaching of salt beds. They have layers of warm water under a fresh water surface, these layers owing their increased temperature to the absorption of solar heat and to the fact that brine has a lower specific heat than fresh water. The surface of Black Lake has a temperature of 21°C., the warm layer below rising to 56°C.[1]

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[1] **A. Kaleczinszky,** Über die ungarischen warmen und heissen Kochsalz Seen, etc., Budapest, 1902. This phenomenon has been previously referred to.

The water of Illyes Lake has a salinity of 233.747 permille, that of Black Lake of 195.3 permille. The composition of the salts is essentially similar. The analysis of Illyes Lake is given in the first column.

Iletsk Lake, Russia.—In the second column is given the analysis of the salt lake near Iletsk, in the southern part of the province of Orenburg, Russia, approximately in latitude 51°N and longitude 55°E on the great plain to the north of the Caspian. There are large deposits of salts in the neighborhood; some were formed by the Caspian Sea at a former higher stand, while others are of greater age. One of these especially, of Permic age, occurs at Iletz Kaier Zachteta, 40 miles south of the city of Orenburg and has an estimated area of one square mile and a thickness of more than 500 feet. This or similar salt beds may have furnished the brine.[1]

There is a remarkable correspondence in the analyses of the waters (Col. 1 and 2) of two such distant lakes as Illyes Lake, Hungary, and Iletsk Lake, Russia, which clearly suggests their similar origin. A comparison with the waters of the Dead Sea shows some very striking differences.

Elton Lake, Russia.—In the third column of Table XXXVII, is given the analysis of Elton Lake, Russia (also called Altan-nor, Jalton or Jelton lake which means shining or glittering lake from the reflection, due to its salt surface). This lake lies on the level steppe north of the Caspian (Fig. 59, p. 130), of which it was formerly a part as shown by the molluscan shells found in the sands of the steppe. It lies about 135 kilometers S. E. of the city of Kamyschin on the Volga, and is of oval form, 18 km. long, 14 kilometers wide (east and west), and has a circumference of 50 km. with a surficial area of 288 square kilometers. Its depth is so slight that one can wade through its entire width. Several kilometers from shore its depth is seldom more than 0.7 meters, but the depth in its central portion is still unknown. It increases in size somewhat from the melting of snows in spring and from October rains, but on the whole its surface remains stationary, although numerous small streams carry salt water into it and the lake is without outlet. This shows that evaporation balances the influx of water and from this it follows that the salinity of the water is constantly on the increase.

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[1] See P. Krusch, Nutzbare Lagerstätten Russlands, Zeitsch. für Prakt. Geol., 1897, pp. 281–283; Eng. and Min. Jour., March 7, 1903, p. 373; Harpers Magazine, Vol. 76, 1888, pp. 904–910; C. Schmidt, Mem. phys. Chim. St. Petersburg, Vol. 11, 1882, p. 602.

The total amount of salt carried annually into this lake is 19,500 metric tons.[1] The newly added water redissolves some of the salts from the bottom of the lake, so that this salt bed is always covered by a brine which is more saline than the water brought in.

In the following table analyses of ten of the streams entering the lakė and 3 analyses of the lake water are given in terms of salts.

TABLE XXXVIII.—ANALYSES, IN TERMS OF SALTS, OF WATERS OF ELTON LAKE AND TRIBUTARY STREAMS AND OF BASKUNTSCHAK LAKE

Parts per 100 of solution

	Charisacha (stream)	Gorkoi-Jerik (brook)	Elton Lake			Baskuntschak Lake	
			I	*II*	*III*	*I* Erdmann	*II* Göbel
NaCl	4.0650	1.6834	7.135	13.124	3.83	21.576	18.9997
KCl	....	....	....	0.222	0.23	....	0.1992
$MgCl_2$	0.5200	0.1646	16.539	10.542	19.75	4.863	5.4349
$CaCl_2$	....	0.2068	....	....	....	0.855	0.9889
Na_2SO_4	....	....	0.384				
$CaSO_4$	0.1238	....	0.036	....	....	0.074	0.0280
$MgSO_4$	0.2827	....	1.858	1.665	5.32	1.030	
$CaCO_3$	....	....	0.038				
$MgBr_2$	....	....	....	0.007	....	....	0.0065
Organic matter	....	....	0.505				
Water	95.0085	97.9452	73.505	74.440	70.87	71.572	74.3428
Total	100.0000	100.0000	100.0000	100.0000	100.00	100.000	100.0000
Salinity permille	49.915	20.548	259.90	255.60	391.3	284.28	256.572
Specific gravity	....	....	1.208	1.2187	1.2728	1.208	1.2365
At temperature	....	....	?	14°R. 63.5°F.	9.5°R. 53.4°F.	14°R. 63.5°F.	14°R. 63.5°F.

The floor of Elton Lake is formed by a salt deposit of unknown thickness but estimated to have a depth of several hundred feet. In 1805 Göbel sunk a shaft in this lake, 2 kilometers from the shore. At the top he found 42 layers of salt ranging from 2½ to 10 cm. in thickness. Below this the salt became more compact and firmer and occurred in layers up to 42 cm. in thickness.. After 58 more layers, a bed of salt was encountered which had such a compactness that the tools were broken by it. This occurred at a depth of 12 feet (about 4 meters), thus giving an average thickness for the 100 salt layers of 4 cm.

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[1] Führer, F. A., Salzbergbau und Salinen-kunde Braunschweig, 1900, p. 17.

In spite of the large amount of magnesium chloride found in the brine of this lake, deposits of this salt seem to be scarce. This is to be attributed to the greater solubility of the $MgCl_2$, which remains in solution and so increases in amount from year to year, even though the quantity brought in by the streams is only from one-eighth to one-tenth that of sodium chloride. As will be seen from the table on p. 22, the solubility of $MgCl_2$ is half again as great as is that of NaCl, and from the experiments of Usiglio and Van't Hoff, it follows that the $MgCl_2$ is mainly retained in the mother liquor.

During the last 150 years, eight and one-half million tons of salt have been removed from this lake and there seems to be no appreciable diminution in the total quantity. There appears to be a sufficient quantity of salt in this lake to supply all of Russia with salt for a long time to come. The means of communication are, however, inadequate.

An analysis of the salt shows the following composition.

TABLE XXXIX.—ANALYSIS OF SALT OF ELTON LAKE

NaCl	96.59
KCl	0.04
$MgCl_2$	0.13
$CaSO_4$	1.01
Impurities	0.37
Water	1.87

The salt production at Elton Lake was in round numbers 115,000 tons in 1867; 16,626 tons in 1870; and 9,765 tons in 1880. It has steadily declined, owing to the difficulties of communication. Improvements are, however, planned.

Baskuntschak Lake (Baskunčak or Bogdo Lake).[1]—This lake like Elton Lake lies in the great salt steppes north of the Caspian (see Fig. 59), and like it derives its salt from the re-solution of the salt deposits left by the Caspian at its former higher stand. It lies about 98 kilometers south of Elton Lake but only 53 kilometers east of the Volga at the foot of the hill Bobsoj-Bogdo. This hill is the continuation of a gypsum ridge which descends into the steppe from the gypsum mountain Tschaptschatschi, which also carries rock salt.

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[1] See Hermann Roskoschny, Die Salzseen an der Wolga. Bilder aus dem Südlichen Russland Bibliothek der Unterhaltung und des Wissens, 1891, p. 179, Union. Deutsche Verlagegesellschaft.

The lake has a circumference of 42 km. and an area of about 127 square kilometers. It is a typical playa lake covered only in spring with water to a depth of 0.35 meters, but forming during the rest of the year a solid and extensive salt mass which resembles a bed of ice, on the surface of which are scattered pools of mother liquor. The analyses of the brine are given in Table XXXVIII. From this table it appears that the sodium chloride content of this brine is from 2 to 5 times as great as that of the Elton Lake brine, while the magnesium chloride is only from one-half to one-fourth that of the same lake. As in the case of that lake, the $MgCl_2$ is retained in the mother liquor only pure salt being deposited. The amount of calcium sulphate is almost negligible as it is in Elton Lake, no gypsum beds being produced though gypsum crystals should be formed.

The salt mass of Baskuntschak Lake has been penetrated to a depth of 54 meters, and three important beds were encountered, an upper 6 to 8 meters, a second 2 meters, and a lower more than 10 meters thick. The upper layer alone gave 680,000,000 tons of salt of a very pure quality excelling that of Elton Lake.

The period during which salt can be obtained from this lake is six months, whereas the producing time of the other salt lakes is mostly only three months long, this being therefore one of the best salt producing lakes known. There has in consequence been a constant increase in the production, favored also by the more accessible location of the lake. This is shown by the following figures. The production for 1870 was 21,000 tons; for 1880, 165,000 tons; 1890, 210,000 tons; and 1897, 257,000 tons.

It may here be noted that an extensive salt deposit appears in Tschaptschatschi (Čapčači) hill, a ridge 15 to 20 meters in height and lying 85 kilometers southeast of Baskuntschak Lake and 96 kilometers east of the Volga. This salt deposit is 2½ kilometers long and has an average width of 1 kilometer. It has been penetrated by boring to a depth of 83 meters without finding its bottom. The salt is very pure, containing 96 per cent. NaCl, and is associated with deposits of gypsum. Owing to the dry climate, the salt bed often appears upon the surface. Many salt lakes are fed by waters from this hill which dissolve the salt, but very little of the gypsum.

SUMMARY OF LEACHED CHLORIDE SALTS

We may then summarize the knowledge gained from a study of the lakes mentioned in this section by saying that salt lakes which derive their waters mainly through re-solution of older salt deposits are very nearly pure sodium chloride waters, and the deposits formed from them are practically pure rock salt. Gypsum as well as sodium sulphate are lacking or only sparingly represented, as are also the potash salts. Magnesium chloride, on the other hand, is abundant in some of these waters, chiefly as the result of progressive accumulation of small quantities brought in by the streams. It remains behind in the mother liquor owing to its great solubility. If complete drying of such water were to result, the salt would be overlain by a layer of Bischofite ($MgCl_2.6H_2O$), but the other mother liquor salts would be rare. As we have several times noted, solution by terrestrial waters is a differential one, the most soluble salts, the $MgCl_2$ and $NaCl$, being taken to the virtual exclusion of the others. Nature here performs the process initiated by man in the purification of salts for commercial purposes, but this performance is upon a vast scale and carried on through centuries of time. Some of the potash and other salts, which may be dissolved by the waters, are left behind in the soil and silt through which the solution is carried. It is highly probable that many of the pure salt deposits of older geological periods have originated in this manner.

SULPHATE WATERS FORMED BY SOLUTION OF OLDER SALTS

Lac Ritom, Switzerland.—This lake which lies in Canton Ticino and drains south into Italy, is remarkable in that its lower part is essentially a strong solution of calcium sulphate derived from nearby gypsum beds. Two distinct layers of water are recognizable, differing in salinity, composition, and temperature. The upper, which is merely the water of the rivers which flow into this lake, has a salinity of 0.1225 permille and is therefore essentially a fresh water layer, high in carbonates as well as sulphates. The lower layer has a distinctly higher temperature, being 5.1° at 11 meters depth, and 6.6° at the bottom. It is also denser, its salinity being 2.373 permille at 13 meters depth where it has the composition given in the second column of the following table. With further concentration this lake would redeposit gypsum.

TABLE XL.—COMPOSITION OF LAC RITOM WATERS

	Surface water	Water at 13 meters depth
CO_2	20.00	2.29
SO_4	47.27	69.89
Ca	22.12	22.15
Mg	5.47	4.96
Na	1.22	0.09
K	1.64	0.15
SiO_2	2.28	0.42
$Al_2O_3+Fe_2O_3$	Trace	0.05
Total	100.00	100.00
Salinity in permille	0.1225	2.373

CARBONATE SALTS DUE TO SOLUTION AND REDEPOSITION OF OLDER SALTS

The most important member of this group is carbonate of lime, which is deposited from waters of low salinity in the form of calcareous tufa, or of solid lime rock (stalactite, stalagmite, Mexican onyx, etc.). Calcium carbonate will be held in permanent solution in water only if free CO_2 is present. This is true for pure waters as well as for those in which other mineral substances are dissolved. The neutral carbonate of lime will unite with the free CO_2 to produce the bicarbonate ($CaH_2C_2O_6$) and this is readily dissolved in water saturated with CO_2 gas at the ordinary atmospheric pressure, and a temperature of 10°C. to the extent of 0.88 grams per liter. Thus the maximum salinity produced under ordinary pressure by the presence of $CaCO_3$ in solution is 0.88 permille, which, it will be observed, is higher than the salinity of most ordinary waters in which $CaCO_3$ is the chief mineral constituent. The bicarbonate of lime can be dissolved in pure water at 15°C. to the extent of 0.385 grams per liter, but the normal calcium carbonate is very slightly soluble in non-carbonated waters. According to Fresenius the quantity is 1 part in 10,800 when cold; and 1 part in 8,875 parts of boiling water. This would give in the first place a salinity of 0.092 permille; and in the second of 0.113 permille, figures which are much closer to the normal for fresh waters. T. Schoesing,[1] however, maintains that the amount of $CaCO_3$ soluble in non-carbonated waters at 16°C. is only 0.0131 grams per liter, an amount approximately one-seventh that allowed by Fresenius.

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[1] Compt. Rend., Vol. 74, 1872, p. 1552; Clarke, Data, etc., 3d ed. p. 128.

When carbonated waters are subject to increased pressure above the normal, the amount of CO_2 which they can absorb is increased and the amount of $CaCO_3$ which can be dissolved likewise increases, until the maximum is reached which is about 3 grams per liter.

When other salts, such as sodium and magnesium chlorides or sulphates are present in the water, the solubility of the carbonate of lime is variously affected, both in carbonated and in non-carbonated waters. Thus when carbonated waters hold either of these sulphates in solution in the proportion of 1 to 100 or less, they will take into permanent solution under ordinary temperature and pressure a quantity of pure carbonate of lime ranging from 1.56 to 2 grams per liter. Carbonated waters of this type may therefore have a salinity as high as 12 permille.

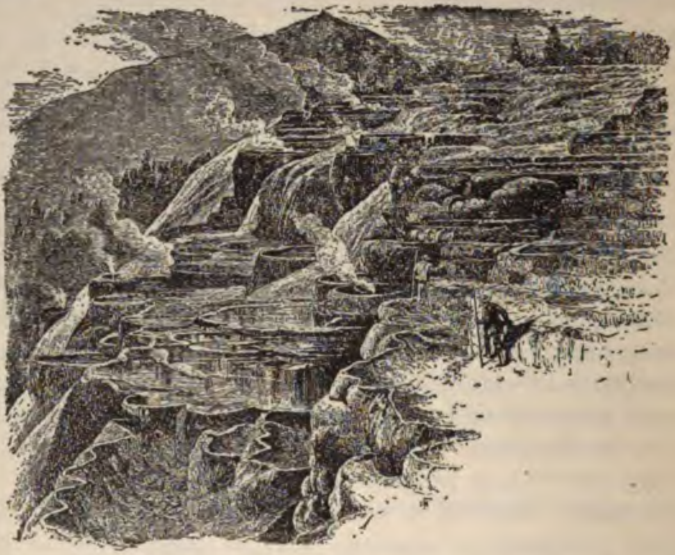

FIG. 73.—View of Mammoth Hot Springs, showing the terraces built of calcareous sinter, and the marginal rims which hold the pools of water. (*After Hayden.*)

When the chlorides of Na or Mg are present in carbonated waters, the formation of unstable supersaturated solutions are favored whenever there is an excess of carbonate of lime present, and this is gradually precipitated out at low temperatures as the hydrous carbonate until the amount in solution is again reduced to 0.8 grams per liter, the normal for carbonated waters under ordinary conditions.

The presence of both chlorides and sulphates of sodium and magnesium in non-carbonated waters likewise favors the formation of unstable supersaturated solutions of carbonate of lime, from which the lime is gradually precipitated. The precipitation is more rapid when the chlorides are present, whereas the sulphates form solutions with a certain amount of stability. Nevertheless, the lime will also be precipitated from the sulphate solutions, this precipitation being complete in from eight to ten days.

The following analyses give the composition of typical calcareous tufas deposited by lake waters and of the travertine of the Mammoth Hot Springs in the Yellowstone (Fig. 73).

TABLE XLI.—ANALYSES OF CALCAREOUS TUFAS

	Mammoth Hot Springs		Lithoid tufa, Lahonton Basin	Calcareous tufa, main terrace, Redding Spring, Great Salt Lake Basin
	A	*B*		
Insoluble	......	......	1.70	
SiO_2	0.09	0.05	......	8.40
Al_2O_3 Fe_2O_3	0.11	0.11	0.25	1.31 Trace
CaO	55.37	52.46	50.48	46.38
MgO	0.35	0.90	2.88	3.54
K_2O	0.04	0.71	......	0.22
Na_2O	.....	0.33	......	0.48
Li_2O	.....	.....	......	Trace
NaCl	0.10	1.45	......	
Cl	......	.....	Trace	
SO_3	0.44	1.82	Trace	
CO_2	43.11	40.88	41.85	38.20
P_2O_5	.....	.....	0.30	Trace
H_2O	0.32	1.02	2.07	1.71
C. (organic)	0.17	0.30		
Total	100.10	100.03	99.53	100.24

In the following table are given analyses of various fresh waters in limestone regions.

TABLE XLII.—AVERAGE COMPOSITION OF THE SALT IN FRESH WATERS OF LIMESTONE REGIONS

	Lake Baikal, Russia	Lake Michigan at St. Ignace, Mich.	Lac Tanay, Switzerland	Danube River above Regensburg, Germany	Mississippi River at Brainerd, Minn.	Magnet Cove Springs, Ark.
CO_3	49.85	49.45	53.21	51.70	51.65	53.59
SO_4	6.93	6.15	5.29	8.54	1.05	3.40
Cl	2.44	2.31	0.87	1.31	0.48	1.35
NO_2	....	.....	.....	0.06		
NO_3	0.21	0.26	.....	0.25		
PO_4	0.72					
Ca	23.42	22.21	33.74	27.40	22.94	30.95
Mg	3.57	7.01	1.99	6.00	4.09	3.45
Na	5.85	4.02	0.75	1.12	5.14	1.08
K	3.44		0.74	0.72	1.75	0.63
NH_4	0.08					
SiO_2	2.03	8.54	2.37	2.42	9.40	5.55
Fe_2O_3	1.46	0.05	1.04	0.06	1.49	
Al_2O_3	.....	....		0.42	2.01	
	100.00	100.00	100.00	100.00	100.00	100.00
Salinity permille	0.069	0.118	0.122	0.204	0.195	0.224

Deposition of the Lime.—Calcium bicarbonate is a very unstable compound and may be broken down into the normal carbonate and pure CO_2. This may be brought about by one or more of the following methods.

1. Evaporation, either partial or complete.
2. Diffusion of the extra molecule of CO_2, which acts as solvent, by:
   - (*a*) Exposure to the atmosphere.
   - (*b*) Relief of pressure.
   - (*c*) Heating.
   - (*d*) Mechanical agitation of the water.

The result is the deposition of the calcium carbonate as a calcareous ooze or as a tufaceous mass.

An example of deposition of calcium carbonate by the evaporation of a large body of fresh water is furnished by the Quaternary Lakes Lahonton and Bonneville in the Great Basin region of western North America. Lake Lahonton (Fig. 74) covered an area of 8,422 square miles mostly in northwestern Nevada, but is now reduced to a number of relatively small scattered sheets of water and many alkaline and saline playas. Lake Bonneville (Fig 68, p. 185) covered an area of 19,750 square miles mostly in Utah, and its chief residuary body is Great Salt Lake. During a former pluvial stage of the climate the basins of these lakes were filled with fresh water, the old shorelines being in many cases still preserved. Carbonate of lime was the chief salt in solution in these waters, and on their evaporation with the gradual aridifying of the climate this was deposited as calcareous tufa. Three types are recognized. These in the order of their age are: (1) the *lithoid tufa*, which is compact and frequently includes the shells of fresh water mollusks; (2) *thinolitic tufa* or *thinolite* (Fig. 75), composed of orthorhombic prisms 6 to 8 inches long and almost half an inch thick; (3) *dendritic tufa* (Fig. 76), usually occurring in mushroom or dome-like masses with a dendritic internal structure. When crowded the masses take on a polygonal outline, like pavement blocks. The deposits of dendritic tufa on the floor of Lake Lahonton may reach in places a thickness of from 20 to 50 feet (Fig. 77, p. 217).

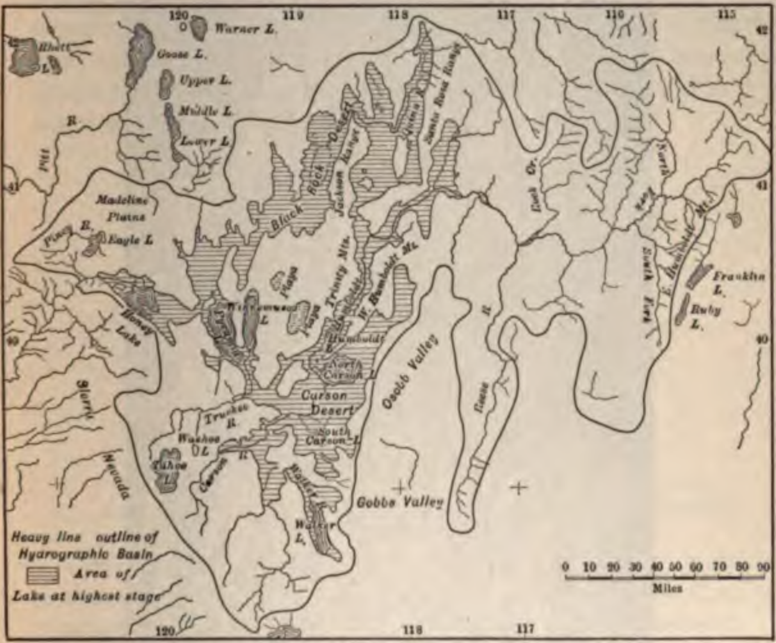

FIG. 74.—Outline map of Lake Lahonton. (*Redrawn after Russell.*)

Deposits of calcareous tufa are likewise formed from river waters in semiarid regions. In Bahia, Brazil[1] horizontal beds

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[1] J. C. Branner, Aggraded Limestone Plains of the Interior of Bahia and the climatic changes suggested by them. Bull. Geol. Soc. America, Vol. XXII, pp. 187-206 (195).

of limestone are deposited by the rivers, which are highly cha
with $CaCO_3$ in solution, having obtained this in their pas
through older limestone regions. Deposition is here due tc
exposure of the water to the tropical sun and the resultant pa
evaporation, but also, and probably in a considerable mea
to the liberation of the extra molecule of CO_2 which holds
lime in solution.

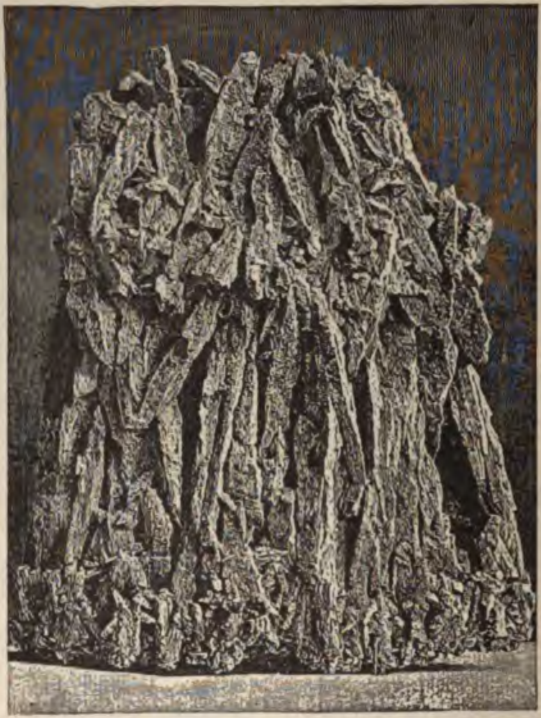

FIG. 75.—Thinolitic tufa from Lake Lahonton. (*After Russell.*)

Elsewhere in torrid America, especially on the margins o
Bolson plains of Mexico, evaporation of the river water, w
at certain times spreads as a sheet flood over the plains, lea
thin, white crust of nearly pure lime on the surface. Th
known as *tepetate* and consists of the lime dissolved from
limestone surfaces in the upper reaches of the river. Si
deposits occur on the great flood plain of the Indus and Ga
rivers of northern India, only here the lime generally forms

cretions which are known as *kankar* and are embedded in the deposits of clastic material.

Springs arising from limestone regions also deposit calcareous tufa often in considerable quantities. The rate of deposition is often very great, a spring at San Filippo, Sicily, depositing tufa at the rate of one foot in four minutes. Such deposits are usually due to the escape of the extra molecule of CO_2, which acts as a solvent of the carbonate of lime. This escape in the case of springs is due partly to the relief of pressure under which the water was held, and partly to progressive diffusion of the CO_2 with exposure to the atmosphere. This diffusion is most rapid where the water is agitated into ripples or otherwise and here the heaviest deposits are sometimes found.

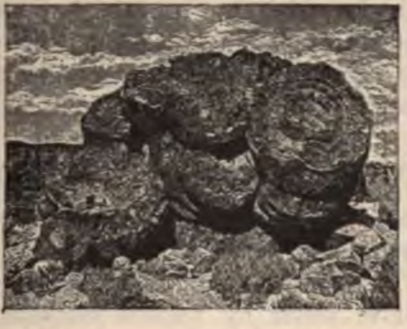

FIG. 76.—Dendritic tufa masses, Lake Lahonton. (*After Russell.*)

The lime salt deposited in caverns in the form of stalactites and stalagmites furnishes another example of the precipitation of this salt by the diffusion of the CO_2 which acts as a solvent. To a slight extent, evaporation of the water in the dry atmosphere of the cavern may also occur, but this is probably of secondary importance.

It should here be emphasized that not all spring waters derive their lime content from solution of older deposits. Many of them, especially thermal springs, may rise from great depths and may be of magmatic origin, the lime content being derived from the igneous magma which gives off the water and not from any previously formed limestone deposits.

CHAPTER XI

SALTS LEACHED FROM DECOMPOSITION PRODUCTS OF OLDER ROCKS. CONCENTRATION OF SALT BY PLANTS

The dissociation of the minerals of older rocks, especially those of volcanic or other igneous types, into their ions by weathering and solution, and the recomposition of these into salts of various kinds, furnish material which terrestrial waters may leach out and concentrate in lakes or ponds where they may be redeposited.

The principal salts which may be classed as derivatives chiefly from decomposition products are the alkaline carbonates, the nitrates, and the alums, though chlorides, sulphates, and carbonates as well as borates are also produced in this manner.

EFFECTS OF ROCK WEATHERING

The weathering of rocks consists essentially of the disintegration of the rock and the decomposition of the minerals which constitute it. This is effected by oxidation of iron compounds, the assumption of water by various substances (hydration); and the leaching out of the soluble bases and the concentration of the less soluble substances, such as alumina and ferric oxide.

From our point of view, the most important result of rock decomposition is the loss which is experienced by the rock, rather than the gain through oxidation and hydration, for it is the substances which are removed in solution which furnish the concentrates from which the salt deposits of this group are formed.

In the following table (from Merrill) the loss in the several constituents of four selected rocks, three igneous and one metamorphic, are given. In order to eliminate the disturbances due to oxidation and hydration the quantity of ferric oxide or of alumina is taken as invariable, since these substances are practically unaffected in the weathering, though not absolutely so. Nevertheless, they may serve as a standard to which the losses in the other constituents can be referred.

In the first of the two tables (XLIII) the percentage of each constituent lost by the original rock is given. The next (XLIV) shows the loss in percentages of the total amount of each constituent originally present in the rock (referred to as 100). Thus in the case of the granite the calcium oxide lost amounts to only 0.81 per cent. of the total rock mass, but it amounts to 25.21 per cent. of the total amount of CaO originally present in the rock, which therefore was 3.21 per cent. of the fresh rock. In the case of the gneiss, the whole of the CaO is lost, which constituted 4.44 per cent. of the original rock.

TABLE XLIII.—LOSSES RESULTING FROM THE DECOMPOSITION OF CERTAIN ROCKS IN PERCENTAGES OF ROCK LOST (AFTER MERRILL)[1]

	Granite	Gneiss	Diabase	Diorite
SiO_2..................	10.50	31.90	8.48	17.43
Al_2O_3.................	0.46	Standard (no loss)	Standard (no loss)	Standard (no loss)
$FeO.Fe_2O_3$............	Standard (no loss)	1.30	2.42	3.53
MnO.................	.....	.....	0.32	
MgO.................	0.36	0.80	0.68	4.97
CaO.................	0.81	4.44	1.83	9.20
Na_2O.................	0.77	2.68	0.50	2.17
K_2O.................	0.85	3.55	0.62	0.21
Pe_2O_5................	0.04	.....	0.08	
Total percentage of rock lost.........	13.79	44.67	14.93	37.51

TABLE XLIV.—THE SAME SERIES OF ANALYSES FIGURED IN PERCENTAGES OF LOSS OF EACH CONSTITUENT (AFTER MERRILL)

	Granite	Gneiss	Diabase	Diorite
SiO_2..................	14.89	52.45	18.03	37.31
Al_2O_3.................	3.23	Standard	Standard	Standard
FeO, Fe_2O_3...........	Standard	14.35	18.10	21.03
MnO.................	.....	.....	41.57	
MgO.................	1.49	74.70	21.70	97.17
CaO.................	25.21	100.00	25.89	97.30
Na_2O.................	28.62	95.03	12.83	84.87
K_2O.................	31.98	83.52	29.15	38.75
P_2O_5.................	40.00	.....	11.39	19.87

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[1] Rocks, Rock Weathering and Soils.

No comparison should be made here between the several kinds of rocks, since decomposition was not uniform in all of them, nor were other conditions alike.

Other conditions being equal, the chemical processes going on in the weathering of rocks and production of soils are intensified by high and retarded by low temperatures. Furthermore, both decomposition and subsequent leaching of the soluble products, are reduced to a minimum in arid climates. The presence of decaying vegetation also aids greatly in the decomposition of the rocks. These facts are brought out in the following tables of analyses of soils from Hilgard.[1] The first column (*A*) gives the average composition of 466 soils from the humid regions of the Southern States; the second (*B*) represents the average of 313 soils from the arid areas of California, Washington and Montana.

TABLE XLV.—AVERAGE COMPOSITION OF SOILS FROM HUMID AND ARID REGIONS (AFTER HILGARD)

	A	*B*
	Average of 466 soils of humid regions	Average of 313 soils of arid regions
Insoluble in HCl	84.031	70.565
Soluble SiO_2	4.212	7.266
Al_2O_3	4.296	7.888
Fe_2O_3	3.131	5.752
Mn_3O_4	0.133	0.059
MgO	0.225	1.411
CaO	0.108	1.362
Na_2O	0.091	0.264
K_2O	0.216	0.729
P_2O_5	0.113	0.117
SO_3	0.052	0.041
Water and organic matter	3.644	4.945
Total	100.252	100.399

This table shows the much larger amount of soluble matter present in the soil of arid when compared with that of humid regions where it is constantly leached by rain waters and carried into the sea by the streams. When rain does fall in the arid regions, as it does at more or less infrequent intervals, a large amount of soluble material is encountered by the water, and this is carried to low-lying regions where temporary playa lakes are formed. On the evaporation of the water the salts are deposited together with the fine silt which is carried into the playa basin. Referring again to the table, we may note the large excess of magnesium, calcium, sodium, and potassium oxides in the soils of the arid regions. It is therefore compounds of these bases which we should expect to find most abundant in the concentration products of desert regions otherwise free from connate salts or uninfluenced by volcanic emanations. This is found to be the case when we examine the minerals characteristic of such a concentration product, as indicated by the list of those found in Searle's marsh, given on p. 282.

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[1] E. W. Hilgard, Report on the Relation of Soil to Climate, Bull No. 3, U. S. Weather Bureau, 1892, p. 30.

WATERS CARRYING DECOMPOSITION PRODUCTS

We may next consider the composition of the waters of basins which have derived their saline constituents chiefly, if not wholly, from decomposition products, and then consider the deposits which are formed by such waters. Clarke[1] calls attention to the fact that by the weathering of rocks, carbonates are first formed, as shown by most rivers near their sources. "Under favorable conditions these salts accumulate and they are transformed into or replaced by other compounds only after a long and slow series of chemical reactions. In recently formed bodies of water derived from igneous rocks, carbonates are abundant; but as salinity or concentration increases, the slightly soluble calcium carbonate is thrown down, leaving sulphates and chlorides in solution. If more calcium is available, gypsum is precipitated and the final result is a water containing little except chlorides. The carbonate waters form the beginning, the chloride waters the end of the series. When calcium is deficient in quantity, then mixed waters are produced, in which alkaline sulphates, carbonates, and chlorides may coexist in almost any relative proportion. Waters of mixed type may also be formed by the blending of supplies from different sources, and the contributions of two tributaries may be very unlike."[2]

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[1] Data, etc., p. 177.

[2] *Loc. cit.*

As we have seen (Chapter III), the solubility of salts in pure water is a very different thing from their solubility in water containing other substances. This is shown by the elaborate series of investigations carried on by the Van't Hoff School of Physical Chemists (see Chapter III).

For NaCl the critical saturation is 111 mol. to 1,000 mol. H_2O. For KCl it is 88 mol. to 1,000 mol. H_2O. Either solution by itself deposits no salt as long as it is below this critical saturation point, but so soon as that is surpassed the respective salts are deposited.

Stated qualitatively, the order of deposition is simple: Thus, given a solution, so dilute that it contains ions capable of forming the chlorides, sulphates, and carbonates of sodium, calcium, and magnesium, which are the chief salts derivable from natural waters, we may postulate the following results: "Upon concentration the difficultly soluble carbonates of calcium and magnesium will be precipitated first, to be followed by the slightly soluble gypsum. Next in order, sodium sulphate and carbonate will form, and these salts are deposited by many saline or alkaline waters. Later, sodium chloride and magnesium sulphate may crystallize out, leaving at last a bittern containing the very soluble chlorides of calcium and magnesium. [However] every step is not necessarily taken in every instance. All of the calcium may be eliminated as carbonate, leaving none for the formation of other salts. All of the sulphuric ions may be taken to produce gypsum and then no sodium sulphate can form. In short, the actual changes which take place during the concentration of a special water depend on the proportion of its constituents and vary from case to case."[1]

The Lahonton Basin (Fig. 74, p. 209).—Of the American regions, the basin of the ancient Lake Lahonton furnishes the most extended examples of residual water bodies rich in decomposition salts. The saline lakes in this basin have no definite relation to the original fresh water lake which occupied it, though in a sense they are the residual legatees of that lake. Nevertheless, the decomposition salts in these residual bodies are probably in large measure, if not wholly, derived from the decomposition of the rocks of the basin, since the disappearance of the fresh water lake, through the aridification of the climate Some of them are, however, more or less influenced by salts of connate and other origin.

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[1] Clarke, "Data of Geochemistry," 3d ed., p. 178.

There are a number of other water bodies of this type, which lie just outside of the old basin of Lake Lahonton, but from their essentially similar character to the residual lakes of this basin may be included in this discussion. Chief among these are Mono Lake and Owen's Lake in California. (See Fig. 92, p. 263.)

The rocks of the Lahonton basin are predominantly of the igneous types, rhyolites and andesites being especially abundant. It is from these that the alkalies are probably in large measure derived. There are, however, sediments of both continental and marine types, exposed within the drainage area of the basin, and it is highly probable that the latter have furnished at least a part of the chlorides from connate salts.

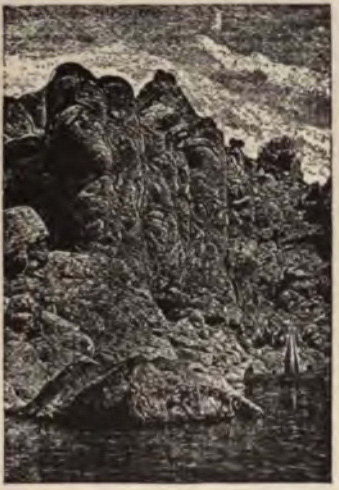

FIG. 77.—Domes of Dendritic tufa. Pyramid Lake, Nevada—former Lake Lahonton. (*After Russell.*)

One further complication exists in this basin, and that is the occurrence of a not inconsiderable number of hot springs. These are probably to be considered in part at least as of magmatic origin, and they supply certain elements which would normally be lacking in waters whose saline characters are wholly derived from decomposition products. The boron of Searle's marsh (Borax Lake) has been regarded as derived from a magmatic source but a marine (connate) source has also been claimed for it. Such an origin is, however, highly improbable. Finally, as in all complex waters and in waters carrying only connate salts, a certain amount of chemical reaction takes place and new salts will be deposited. That such occur in the basins under discussion is beyond doubt, and some of them will be referred to later.

Other Areas Characterized by Waters Rich in Decomposition Products.—In the Canadian extension of the Great Basin region are situated many other water bodies which carry decomposition products derived from igneous rocks of the region. As in the case of the Lahonton basin, these water bodies lie in the region of westerly winds, which are intercepted by the Rocky and other mountain ranges and so produce arid or semi-arid conditions upon their eastern sides. Other typical examples of such lakes abound in many of the steppes of Siberia and in other parts of Asia as well, though we are less familiar with the rocks of these regions. The same is true of the Kalahari Desert of the interior of South Africa, and some of the desert regions of South America. Finally, special conditions exist in the eastern Sahara Desert where, as in Natron Valley, decomposition products are modified to a large extent by products resulting from the leaching of sedimentary rocks and the formation of new products by chemical reactions.

In the following discussion we shall consider in turn the waters of similar chemical character, rather than attack the problems from a geographical basis.

LAKES IN WHICH THE WATERS ARE PREDOMINANTLY CHLORIDES WITH SODIUM AS THE CHIEF BASE

The following analyses of waters from the Lahonton Basin (tabulated by Clarke) show those lakes in which the water contains predominantly sodium chloride, while the affluents are rich in calcium carbonate.

Comments on the Analyses.—In commenting upon these analyses the relationships of the various members of each series must be kept in mind. In Series *A* we have a complete inward drainage system beginning with Lake Tahoe, a mountain lake lying partly in California and partly in Nevada, and having an elevation of 6,225 feet with a depth of 640 feet. It is largely surrounded by igneous rocks, but there are some areas of marine

TABLE XLVI.—ANALYSES OF CHLORIDE WATERS FROM LAHONTON BASIN

	Series *A*				Series *B*		Series *C*	
	Lake Tahoe, Cal.	Truckee River, Nev.	Pyramid Lake, Nev.	Winnemucca Lake, Nev.	Walker River, Nev.	Walker Lake, Nev.	Humboldt River, Nev.	Humboldt Lake, Nev.
Cl	3.18	7.59	41.04	47.88	7.50	23.77	2.19	31.82
SO_4	7.47	12.87	5.25	3.76	16.14	21.29	13.92	3.27
CO_3	38.73	33.30	14.28	7.93	30.34	17.34	39.55	21.57
PO_4	.....	......	......	.....	......	.....	....	0.07
Na	10.10	17.26	33.84	36.68	18.07	34.83	13.63	29.97
K	4.56		2.11	1.94			2.92	6.54
Ca	12.86	11.02	0.25	0.55	12.96	0.90	14.28	1.35
Mg	4.15	3.49	2.28	0.49	2.21	1.56	3.62	1.88
SiO_2	18.95	14.47	0.95	0.77	12.78	0.31	9.51	3.53
Al_2O_3	.....		.....	.....	......	.....	0.38	
Fe_2O_3	.....							
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille	0.073	0.153	3.486	3.602	0.180	2.500	0.361	0.929

(?) Triassic rocks in the neighborhood. This lake drains through Truckee River into Pyramid and Winnemucca Lakes, two bodies of enclosed waters in Western Nevada, likewise situated in the midst of a country of igneous rocks.

The first thing which will be noted in the change of the waters of this drainage system is the great increase in chlorides in the terminal lake and the corresponding decrease in the carbonates. Carbonate of lime is thrown down in the form of thinolitic tufa, but this hardly accounts for the great proportional increase in sodium chloride which approaches that of normal saline lakes. Evidently there seems to be some supply of salt from connate sources or older salt beds, which in the case of Winnemucca Lake may be from bordering Triassic deposits, but is not so clear in the case of Pyramid Lake. The existence within the lake of a number of hot springs which form deposits of calcareous tufa beneath the surface of the lake, may in part account for its salinity. Fish and mollusks abound in it.

Walker Lake in Esmeralda County, western Nevada, lies in a valley bordered by ranges of igneous rock which rise 4,000 feet or more above it, and it is fed by Walker River, which for part of its course passes through a deposit of Tertiary beds probably of continental origin. Nevertheless, the high content of sodium chloride in Walker, as in Pyramid and Winnemucca Lakes, suggests an addition of salts from connate or other sources.

Humboldt Lake in northern Churchill and southern Humboldt Counties, Nevada, lies in an arm of the Carson Desert, where Carson River from the south dwindles away in the playas of Carson Sink. Humboldt River enters the valley from the north but dwindles away as a rule before reaching the lake. This river contains a much higher percentage of calcium and magnesium carbonate and sulphate than is found in the lake water. In this the content of sodium chloride is less than in the preceding lakes, though still very high. The high percentage of the CO_3 ion in this water is notable, while calcium is also present in much larger quantities than in the other lake waters. Of special interest is the high percentage of potassium which on the evaporation of the water would give a mother liquor unusually high in this substance.

LAKES IN WHICH THE PREDOMINANT SALTS ARE SULPHATES

Sulphate waters, especially those in which sodium sulphate predominates, are of frequent occurrence in the modern desert areas, especially those situated in the midst of rocks of other than marine origin. Calcium and magnesium sulphates, on the other hand, are, as we have seen, common in waters of marine origin and may to a certain degree be derived from connate sources as well as from the leaching of older deposits. Thus, as we have seen, sodium sulphate is deposited in the Karabugas Gulf, the waters of which are primarily concentrated sea water though modified by the influx of other salts from the land. Sodium sulphate is also deposited by Great Salt Lake and Sevier Lake (p. 187), the salts of whose waters are principally of connate origin. Nevertheless, it is probably true that sodium sulphate is often chiefly a decomposition product and is probably most abundant in waters of desert regions, surrounded by igneous rocks. In the following table, analyses of waters situated in such regions are given. As sodium sulphate is more soluble in warm than in cold waters, its precipitation is more frequent in winter than in summer, or in cold regions than in those of higher temperature.

The following table gives analyses of such waters from playa lakes of Wyoming, Russia, and elsewhere.

TABLE XLVII.—ANALYSES OF SULPHATE WATERS FROM AMERICAN AND RUSSIAN LAKES

	Wyoming			Canada	Siberia									Mexico
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*	*M*	*O*
	Track Lake	Red Lake	Lake DeSmet	Chaplin Lake, Saskatchewan	Lake Altai	Lake Biljo	Lake Domoshakovo	Lake Tagar	Lake Schunett	The Kisil Kul	Issyk Kul	Barchatow Bitter Lake	Bülüktü Kul	Chichen Kanab, Yucatan
Cl	2.74	3.06	0.90	4.98	14.38	9.91	3.71	29.52	38.89	48.28	15.64	45.05	37.96	8.14
Br	.....	.....	.....	.....	Trace	.....	Trace	Trace	.....	Trace	0.03	0.11	0.04	
SO₄	64.30	64.57	64.15	61.86	50.14	52.33	63.62	34.99	32.19	14.55	55.94	20.23	27.39	58.64
CO₃	.....	.....	5.14	1.54	1.12	6.22	0.08	1.55	0.31	0.22	1.26	.....	0.98	
B_4O_7	1.14	0.57												
PO₄	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.02			
NO₃	.....	.....	.....	.....	.....	1.07	0.07							
Na	30.20	29.89	20.85	30.65	32.83	21.83	30.61	28.41	16.12	34.01	11.76	28.01	23.29	11.99
K	.....	.....	1.27	Trace	0.52	0.87	0.59	1.01	0.33	0.35	1.85	0.26	0.32	0.43
Ca	0.53	0.59	1.10	Trace	0.05	0.43	0.58	0.27	0.44	0.69	0.94	.....	5.28	13.49
Mg	1.09	1.32	6.32	0.97	0.90	7.28	0.74	4.12	11.67	1.86	12.50	5.84	4.68	7.31
SiO₂	.....	.....	0.22	Trace	0.03	0.03	Trace	0.04	0.01	0.04	0.06	.....	0.06	
Al₂O₃	.....	.....	0.05	Trace	0.02	0.03	Trace	0.09	0.09					
Fe₂O₃	.....	.....		....	0.01	.....	.....	.....	.....	Trace	Trace			
S. sulphide	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.50		
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille	77.30	93.10	6.708	27.30	108.8	8.8	145.5	20.9	151.9	108.7	3.574	13.308	11.458	4.446

Comments on the Analyses

The first two lakes are known as the Laramie lakes or playas. The other two are normal water bodies of moderate salinity. Chaplin Lake lies near the station of that name on the Canadian Pacific in southern Saskatchewan. The lakes numbered *E* to *J* are in the government of Yeniseisk on the Siberian steppes. They lie on both sides of the Jenissei River, as shown in the map (Fig. 80, p. 228.) They all belong to the group of playa lakes formed as shallow depressions in the broad surface of the steppe. Barchatow Bitter Lake (*L*) is 300 versts southwest of Barnaul, Government of Tomsk, Southern Siberia; while the last Russian lake is in the Kirghiz steppes southern Siberia, where is also located Issyk-Kul at an altitude of 5,300 feet A. T. The origin of the saline constituents of all of these lakes is so far as we know primarily due to decomposition of igneous rocks. Connate salts and older salt beds may, however, produce a part of the salinity.

THE AMERICAN SULPHATE LAKES

The Laramie Lakes.—The two Laramie Lakes (*A*, *B*) of Wyoming are playa lakes, frequently entirely dry and forming crusts of sodium sulphate with some chloride.[1] Lake De Smet, Wyoming and Chaplin Lake, Saskatchewan, Canada, are very similar in composition, though much lower in salinity. Lake De Smet also carries some carbonates and a considerable proportion of magnesia.

"Upon the Laramie plains[2] there are no less than one hundred slight depressions containing more or less alkali. In the majority of cases the alkali is found in the fall of the year in a thin crust upon the bottom of small ponds which have recently dried up, ... in the early spring and often in the late summer the deposits are covered with water [which] accumulates through the melting snows and rains [and] is often a foot or more in depth; but beneath this one can find a solid bed of crystallized alkali. Later in the season, these so-called lakes are deposits of snow-white alkali, which when seen from a distance resemble a snow-covered basin.

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[1] L. C. Ricketts, Ann. Rept. Territorial Geologist, Wyoming, 1888, p. 45. A. R. Schultz, Bull. U. S. Geol. Surv. 430, p. 570.

[2] W. C. Knight and E. E. Slosson, Alkali Lakes and Deposits, Bull. Wyo. Exper. Sta. No. 49, 1901, pp. 84–88.

"The deposits vary in size from a few to 100 acres and in thickness from a few inches to 10 or possibly 15 feet. The salts are always found resting upon a muddy bed, which is usually very soft, and without difficulty one can force a pole to 5 or 6 feet below the hardened deposit. The mud varies in color from almost black to bluish, and contains many crystals of sodium sulphate. When it is removed from the bed it has a strong odor of sulphureted hydrogen, and often one is conscious of an odor resembling that arising from dissolving sodium hyposulphide. This mud always contains quite a percentage of salts found in the deposits."[1] (Fig. 78).

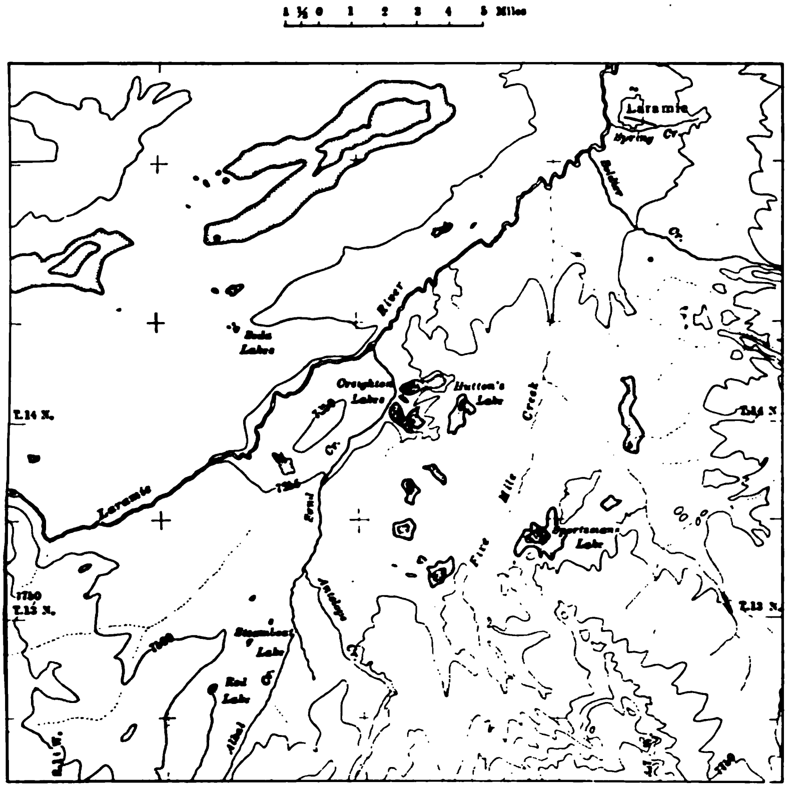

FIG. 78.—Map of Laramie plains and lakes. (*U. S. G. S.*)

According to Knight, the beds are never pure but consist of alternating layers of salts, sand, and mud. The sand and mud are generally spread over the layer of salt by winds during the winter, and to some extent by the streams in spring, which also bring in the salt in solution. As a rule "the deposits are mixtures of the various salts arranged in bands of varying thickness and alternating with other bands containing large percentages of sand or mud." An average sample of the salt from the Laramie or Union Pacific lakes (see analyses of water in columns *A* and *B*, Table XLVII), gave the results shown in Table XLVIII, column *A*.

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[1] Knight and Slosson, *Loc. cit.*

Others of these alkali lakes range high in magnesium sulphate and still others are largely sodium carbonate.

TABLE XLVIII.—ANALYSES OF SALTS FROM LAKES OF WYOMING

	A	*B*	*C*	*D*	*E*	*F*	*G*
Sodium sulphate	75.63	93.07	19.67	12.13	24.40	6.85	14.75
Sodium chloride.	.....	.....	0.50	0.38	17.71	0.05	2.66
Sodium carbonate..........	.....	.....	.....	......	59.00	47.18	59.55
Calcium sulphate........	1.46	2.01					
Magnesium sulphate........	0.70	1.43	30.03	42.34			
Magnesium chloride......	3.00	4.16					
Sodium borate..	1.21	0.75					
Insoluble.......	.....	.....	0.51	0.65	.....	0.71	3.06
Water..........	.....	.....	49.29	44.50	.....	45.21	53.87
Total........	82.00	101.42	100.00	100.00	101.11	100.00	133.89

A and *B*, Dry salts from the Laramie or Union Pacific Lakes, Albany County.

C, Salt from Downey Lake, Albany County, calculated as dry salt it contains 59.82% $MgSO_4$, 39.18 Na_2SO_4, and 1.00% NaCl.

D, Salt from Rock Creek group, Albany County, calculated as dry salts this gives Na_2SO_4 22.13%, NaCl 0.69%, and $MgSO_4$ 77.18%.

E, Dry salt from Wilmington Lake, Natrona County.

F, Omaha Lake, Natrona County, calculated as dry salt Na_2SO_4 12.67%, NaCl 0.09%, Na_2CO_3 87.24%.

G, Borthalton Lake, Natrona County, best deposit, calculated as dry salt Na_2SO_4 34.27%, NaCl 6.16%, Na_2CO_3 59.57%.

In the fall, when the surface of the playas is dry and unprotected it often becomes a powdery mass from which the winds carry away large quantities. Sometimes the air is so filled with dry soda salts that from a distance of 4 or 5 miles it seems filled with white smoke and steam from a great fire. When in the fall the wind blows 40 to 60 miles an hour, the alkali dust rises 50 to 100 feet above every alkali playa. Thus much is carried away and reincorporated in the soil from which the spring rains wash it out again in solution.

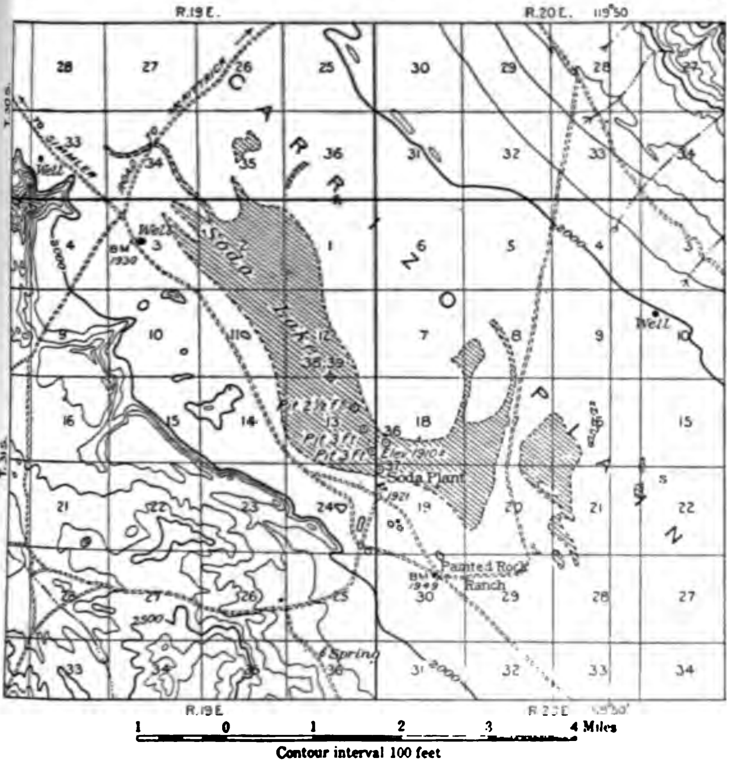

FIG. 79.—Map of Soda Lake in Carrizo plain, Cal. (*After Gale.*)

The source of these salts was formerly believed to be in springs which fed the lake, but Knight's extensive study indicates that it is all supplied by leaching from the neighboring strata. These are the Triassic and Tertiary strata (more rarely the Cretacic) which are older continental beds, the former especially being an ancient desert deposit. These salts exist in a more or less diffused condition in these rocks, having been originally derived from decomposition of the igneous rocks. No extensive beds of these salts are, however, known in these older sediments.

Soda Lake, California.—In southeastern San Luis Obispo County, California, between high parallel mountain ranges, lies the flat-bottomed desert valley known as the Carrizo plain, which with an average width of 4 to 5 miles has an elevation ranging from 1,910 to 2,000 feet. The valley is a graben, faulted down between the Coliente and Tembler ranges, movements of very recent date being indicated along the margins. The surface of the fault block is covered to an unknown depth by gravels and sands of Pleistocenic and perhaps earlier date, washed by the streams from the bordering mountains (Fig. 79). In these mountains occur large areas of soft conglomerates, sandstones, and shales, chiefly of Tertiary age, from which soluble salts have been leached out and concentrated on the valley bottom.[1]

On the lower portion of this plain lies Soda Lake, a desert playa with an area of 2,800 to 3,000 acres. Flooded only during storms, this playa is normally a broad, flat plain of white crystalline salt, ranging from a thin sheet about the margins, to a deposit a few inches thick in the deeper portions, with occasional local channels in which the deposit is thicker. The salt is nearly pure sodium sulphate, as is shown by the following analysis.

TABLE XLIX.—ANALYSIS OF SALINE CRUST FROM SODA LAKE, CAL.

Insoluble	0.40
Al_2O_3	0.04
MgO	1.66
CaO	0.45
Na_2O	40.50
K_2O	0.28
H_2O	3.65
CO_2	None
SO_3	46.12
Cl	9.27
	102.37
Less oxygen	2.09
	100.28

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[1] Ralph Arnold and H. R. Johnson, Sodium sulphate in Soda Lake, Carrizo Plain, San Luis Obispo County, Cal.; Bull. U. S. Geol. Surv. No. 380, 1909, pp. 369–371.

Hoyt S. Gale, Sodium Sulphate in the Carrizo Plains, San Luis Obispo County, California, Bull. U. S. Geol. Surv. 540-N, pp. 32–37.

This would give 81.86 per cent. of anhydrous sodium sulphate, and 8.97 per cent. of sodium chloride.

Where solutions and fractional crystallization takes place, crystals of Mirabilite ($Na_2SO_4.10H_2O$) separate out.

Under the surface crust lies a soft mud of dark greenish or grayish-black color, containing salt in crystals and solution. Embedded in the mud are a number of flat, tabular crystals of clear glassy Bloedite or Astrakanite ($Na_2SO_4.MgSO_4.4H_2O$). Whether or not lower salt beds exist has not been ascertained. Estimating the specific gravity of the salt of the crust at 1.75, its average depth at 2 inches and the surface area at 2,800 acres, the total amount of crude salt in this playa is over a million short tons (Gale).

Lake Chichen Kanab (Little Sea). This lies in Yucatan and is remarkable because of the high percentage of Ca which is present, which exceeds that of the sodium. This lake deposits gypsum, but the source of its salts is not altogether clear. It may be derived from solution of gypsum beds in the vicinity, in which case it belongs to the class of lakes discussed elsewhere as deriving their mineral matter from such sources. It stands alone as a separate type.[1] According[2] to Dr. J. J. Galloway this is a fault block lake, and it may be fed by springs arising along the fault surface.

THE RUSSIAN SULPHATE LAKES

Of the numerous Russian lakes with water predominantly carrying sulphate salts, the following may be considered more at length, Lake Altai, Lake Domoshakovo, Lake Tagar, The Kisil-Kul, and Lake Schunett. The localities of some of these are shown on the map, Fig. 80. Analyses of their water are given in Table XLVII.

Lake Altai.—Lake Altai[3] lies in the Abakanskian Steppe, in the southern part of the Siberian Government of Yenisseisk, and is a typical example of a sodium sulphate depositing lake. It is nearly round in form and has a diameter of about 1 kilometer when its depth is between 70 to 80 cm. Its floor is covered

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[1] J. L. Howe and H. D. Campbell, Examination of Specimens from Chichen Kanab, Yucatan, Am. Jour. Sci., 4th Ser. Vol. 2, 1896, pp. 413–415.

[2] Private communication.

[3] Von Buschman, Das Salz, Vol. II, p. 132.

F. Ludwig, Zeitsch. f. Prak. Geologie, XI, 1903, p. 404.

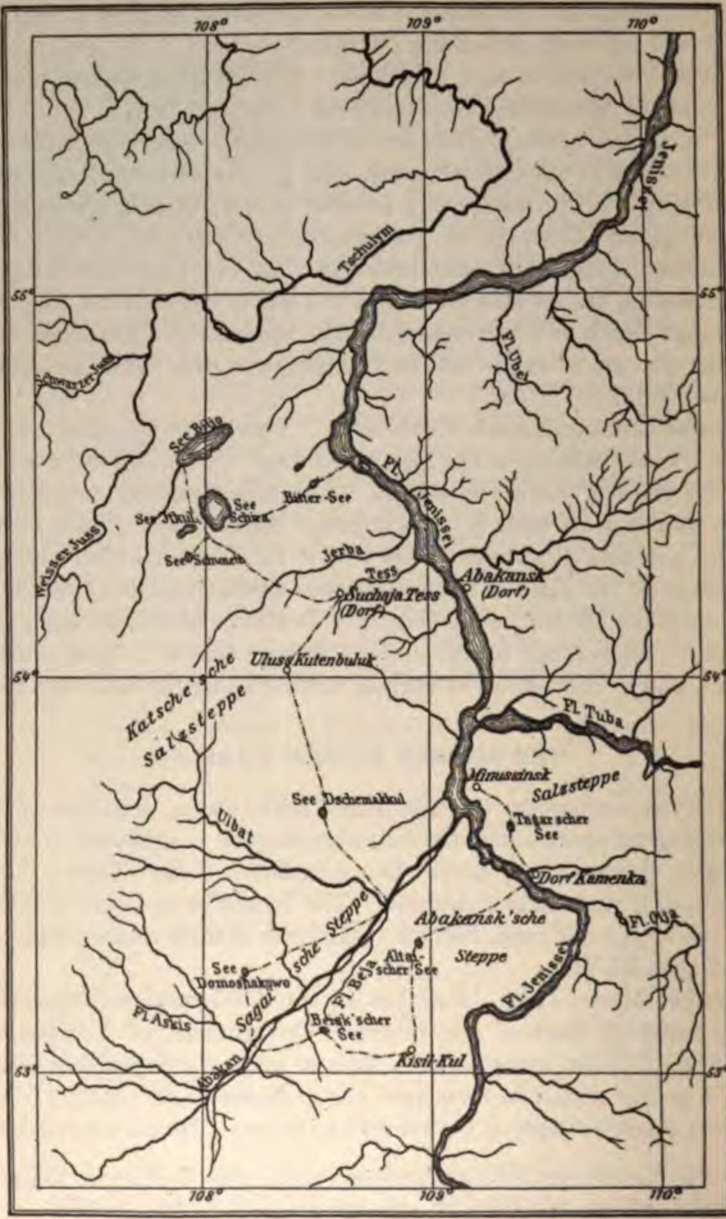

FIG. 80.—Map showing the location of the principal Russian sulphate and other lakes. (*After Ludwig.*)

by a thick deposit of salts, known generally in Siberia by the name of "Busun." This is about ¼ meter in thickness, and so solid that one can walk upon it. It rests upon a substratum of black inorganic mud, below which are other strata of Busun and mud layers. The shores are covered by masses of snow-white salt, consisting of weathered Busun, which has been washed ashore. In the following table are given analyses of the water in parts per thousand, and of the salts. In spite of the high sodium sulphate content, ordinary salt (NaCl) has been manufactured here at considerable expense but this is possible only in autumn and winter when the glauber salts separate out under the influence of the cold and settle to the bottom of the lake. The glauber salt is very pure and is extensively used in the neighboring glass factories.

TABLE L.—ANALYSES OF WATER OF LAKE ALTAI AND OF THE NATURAL SALTS DEPOSITED BY IT

	Salts of lake water in parts per 1,000 (permille)	Salts (Busun) deposited by the lake waters, amounts in 100 parts of anhydrous salts (per cent.)	
		From bottom of lake	From shores of lake
$MgBr_2$	0.0009		
$CaCO_3$	0.0545	0.1268	0.0193
$CaSO_4$	0.1202	0.3498	0.0012
$MgSO_4$	0.4887	0.3329	
K_2SO_4	1.2720		
Na_2SO_4	78.9053	95.1251	98.8471
NaCl	25.7712	0.2914	0.1346
Na_2CO_3	2.1083	0.1514	0.0518
SiO_2	0.0334		
Al_2O_3	0.0212		
Fe_2O_3	0.0092	0.1106	0.0061
Insoluble in HCl. Organic residue	....	1.1228	0.7548
Inorganic residue	....	2.3332	0.1582
	108.7849	99.944	99.9731
Sp. Gr. at 15°C	1.0948		

The residue remaining on evaporation at 180°C. constituted 108.5954 permille. The half combined CO_2 in the water was 0.0240 permille.

Lake Biljo.—This is the largest of the group of salt lakes in the Yenisseisk region, having a circumference of 60 kilometers. Its salinity is, however, very low compared with that of the others, being only 8.8 permille. It is a moderately alkaline water. At 15°C. its density is 1.0079.

Lake Domoshakovo.—Lake Domoshakovo is essentially a solution of sodium sulphate, with very little else. It deposits that salt in considerable quantity.[1] This lake is situated in the Katsche salt steppe of East Siberia and has a length of about ½ and a width of about ¼ km. with a depth of only ¼ meter. The water, an analysis of which is given above, has a specific gravity of 1.344 at 15°C.

The shores of the lake are clayey and moist for some distance. Beneath the water is a solid bed of "Busun" capable of supporting the wader. In very dry summers the lake dries up completely, exposing the layer of Busun which is about ¾ meters thick. The following table gives the analysis of the deposit and its combination into salts after Ludwig.

TABLE LI.—ANALYSIS OF SALTS FROM LAKE DOMOSHAKOVO, SIBERIA. IN 100 PARTS OF ANHYDROUS SALT

Radicals		Calculated as salts	
CO_2	0.1136	$CaCO_3$	0.1622
CaO	0.5800	Na_2CO_3	0.1017
SO_3	55.3129	NaCl	0.1405
Cl	0.0852	Na_2SO_4	96.9775
$Fe_2O_3 + Al_2O_3$	0.0435	$CaSO_4$	1.1884
Na	0.0553	$\left.\begin{array}{l}Fe_2O_3\\Al_2O_3\end{array}\right\}$	0.0435
Na_2O	42.4233	.	
Insoluble in HCl.		Insoluble in HCl.	
Organic	0.3760	Organic	0.3760
Inorganic	0.9440	Inorganic	0.9440
	99.9338		99.9338

Lake Tagar.—This is one of a number of salt and bitter lakes situated in the department of Minussinsk in the Government of Yenisseisk, upon an elevated salt steppe upon which there are, however, also some fresh water bodies. It lies upon the right bank of the Yenisseisk (Jenissei) River, 16 kilometers from

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[1] F. Ludwig, Zeitsch. fur Prakt. Geologie, Vol. XI, 1903, p. 407.

Minussinsk, and on account of its fine black mud has been used as a medicinal bath. It is about 1 verst long and ¾ verst broad, with a depth ranging up to 2½ meters in the deepest part. The shores are low and for the most part not forested. The floor consists of mud which also covers the shores. When wet it is black, with a sp. gr. of 2.0742; when dry, gray with a sp. gr. of 2.6766. For the most part it is of the consistency of cold-cream, but contains sand particles. It contains 27.020 per cent. of organic and other substances volatile on heating to a gentle glow. Of the 72.98 per cent. of solid mineral substances remaining, 0.5800 per cent. was soluble in water, 8.6931 per cent. in HCl, and 63.7072 insoluble in either. Analyses of the last two groups gave the composition shown in the first two columns of Table LIII. For analysis of water see Table XLVI, column *H*.

Of the salts derived from evaporation of the water, which is of too low salinity to deposit natural salts, only about one-half is sodium chloride. The rest is chiefly sodium sulphate and some magnesium salts. The percentage of potassium is also very high, though only about half that of the California and Nevada lakes. Only common salt (NaCl) has been manufactured from this lake, and this is no longer done.

The Kisil-Kul.—The Kisil-Kul or Red Lake (from its red shores) lies about 60 km. from the city of Minussinsk, and southeast of Lake Altai (Fig 80). It is a playa which is only occasionally covered by a thin layer of water. The salt deposit here is covered by sediments, but a dense brine is obtained from bore holes made on the shores of the lake. The brine obtained by pumping from a depth of 5 to 10 meters has a density varying from 9 to 12 degrees on the Baumé scale. The salt production here is from 1,500 to 1,800 tons per year.

Lake Schunett.—This lake lies in the northern part of the Katschesch salt steppe, about 90 kilometers northwest of Domoshakovo, and is one of a group of small lakes surrounded by hills (Fig. 80). The lake is small, having a circumference of 3 to 4 km., while its depth is from 1 to 1½ meters. Its shores are formed of mud, which is reported to have a curative effect on rheumatic troubles. A small stream flows into this lake, but this is dry in summer. Near the center, the floor of the lake is covered with a layer of salt which is strongly impregnated with mud and has the following composition.

TABLE LII.—COMPOSITION OF SALT IN LAKE SCHUNETT

$CaCO_3$	0.12	K_2SO_4	3.65
$MgCO_3$	0.14	$MgSO_4$	30.32
Na_2CO_3	1.20	Al_2O_3	0.07
NaCl	0.92	Fe_2O_3	0.01
Na_2SO_4	57.81	SiO_2	0.07
		Insoluble organic and inorganic	5.69
			100.00

In very hot seasons sodium chloride is also separated. The moist mud has the following composition:

Loss in drying at gentle glow (=water, organic matter, volatile substances)	51.8187
Solid mineral substances	48.1813
	100.0000

The composition of the mud is given in the last 4 columns of Table LIII.

TABLE LIII.—ANALYSES OF MUD FROM LAKES TAGAR AND SCHUNETT, SIBERIA

	Lake Tagar		Lake Schunett			
	Insoluble in H_2O, soluble in HCl	Insoluble in H_2O or HCl	Soluble in water	Soluble only in HCl	Insoluble in HCl	Total
Fe_2O_3	0.6420	3.0049	......	0.2729	0.9114	1.1843
P_2O_5	0.0795	......	......	0.1073	......	0.1073
Al_2O_3	0.9045	7.2452	......	0.0996	0.3958	0.4954
CaO	3.1440	3.9175	0.8805	4.5442	4.1093	9.5340
Mg	......	......	0.4667	......	......	0.4667
MgO	0.5169	0.6482	1.6451	4.3383	......	5.9834
SO_3	0.1317	0.1530	4.5220	2.1432	5.8705	12.5357
CO_2	2.8878	......	......	7.0641	......	7.0641
K	......	......	0.1282	......	......	0.1282
K_2O	0.0505	......	......	0.1306	......	0.1306
Na	......	......	2.3863	......	......	2.3863
Na_2O	0.3362	......	......	0.0787	......	0.0787
Cl	......	......	5.1455	......	......	5.1455
SiO_2	......	1.4665	0.2266	......	1.1257	1.3523
SiO_2 (sand)	......	47.2719	......	......	2.4979	2.4979
S	......	......	......	......	0.2341	0.2341
Total	8.6931	63.7072	15.4009	18.7789	15.1447	49.3245

Other Russian Lakes.—The last three of the Russian lakes analyses of which are given in Table XLVII, Issyk Kul, the Barchakow Bitter Lake, and the Bülükü-Kul or Fish Lake, are lakes of comparatively low salinity. The first and last are situated in the Kirghiz steppes, and the second in the Government of Tourhs. They are sulphate-chloride waters and magnesium is comparatively high.[1]

SODIUM SULPHATE DEPOSITED BY SPRINGS

Sodium sulphate is also deposited in the Lahonton Basin by the springs of Mason Valley. These springs range in temperature from about the mean of the region up to 162°F. The water is of low salinity, but on evaporation deposits salts over parts of the desert area. A section of such a deposit is given, by Russell,[2] as follows:

3. White hard crust of sulphate of soda, with common salt, some calcium carbonate, etc. 1–2 inches
2. Soft, mealy or clayey deposit of sodium sulphate, calcium carbonate, calcium sulphate, etc. 2–7 inches
1. Clear, transparent crystals of sodium sulphate with some earthy impurities resting on saline clay. 6–8 feet

It may be argued that these springs are of magmatic origin, and therefore do not belong under the present category. This is possible, especially for the springs of high temperature, but has not been definitely proven. Contributions from vadose sources may affect some of the other waters discussed.

Sodium sulphate (thenardite) is deposited by Rhodes' and Searle's marsh, California (see *postea*), these and the other salts being derived, according to Campbell, by leaching from Tertiary sediments.

LAKES WITH DOMINANTLY ALKALINE WATERS

The name alkaline waters is usually given to waters in which carbonates of the alkalies, especially carbonate of sodium, are of high percentage. The salts of these waters are probably to a large extent decomposition products derived especially from volcanic rocks. They are therefore characteristic of desert areas surrounded and underlain by rocks of this type. The lakes of western Nevada and California and regions farther north furnish characteristic examples. That the decomposition of rocks is not, however, the only origin of the alkaline carbonates is held by students of foreign lakes of this type. The other modes of origin advocated are the reduction of alkaline sulphates, by organic matter (algæ) as is held by E. Sickenberger for the Natron lakes of Egypt (see below), and the double decomposition between calcium bicarbonate and alkaline sulphates or chlorides, a method regarded by some as the most general of all, and first advocated by T. Sterry Hunt. This is the method accepted by E. von Kvassay for the origin of the soda of the Hungarian lakes, and is regarded by G. Schweinfurth and L. Lewin as accounting for most of the soda of the Egyptian lakes, though he admits to some extent the explanations of Sickenberger for these lakes. The sodium carbonate in the soils of arid regions, which on solution rises to the surface by capillarity and forms the crust of alkali, is held by F. W. Hilgard to be due to this same double decomposition between alkaline salts and calcium bicarbonate.

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[1] For other examples see C. Schmidt, Die Seen der "Bittersalzlinie" von Omsk bis Petropawlowsk und der "Sibirischen Kosakenlinie," von Petropawlowsk bis Präsnowskaju. Mem. Acad. St. Petersburg, Vol. 20, No. 4, 1873.

[2] Geology of the Lahonton Basin, p. 48.

One of the most significant sources of origin of alkaline waters, and one which may play a rôle in nature of greater importance than is now recognized, is found in the exchange of bases which takes place when waters carrying carbonate or other salts of lime or magnesia come in contact with sodium aluminum silicates, *i.e.* sodium zeolites. Although this power of exchange of bases had been known for more than half a century to be characteristic of zeolites, it was not until 1905 that the subject was fully investigated by Professor Robert Gans, Director of chemistry of the German Geological Survey. His attention* was first drawn to the subject by noting that waters originally hard would become completely softened by passing through certain soils of volcanic origin and on thorough investigation of these soils he found them rich in zeolites of more or less similar composition. He found further that an artificial zeolite of constant composition gave the best results. This substance under the name of "Permutit" is now extensively used for softening of water by filtration. It will be seen that waters high in sodium carbonate may be produced by the constant filtration of waters carrying lime and magnesium carbonate through volcanic rocks abounding in such zeolites. The reactions are as follows:

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* Jahrbuch der Kgl. preussischen Geologischen Landesanstalt, 1905–1906. My attention was called to this matter by Professor D. D. Jackson of Columbia University who has briefly discussed it in an article entitled "Water softening by fitration through artificial zeolite." Journ. Am. Water works association Vol. 3, no. 2, June 1916, and other papers.

$$\begin{aligned}
\textit{Sodium zeolite} + \textit{Calcium salt} &= \textit{Calcium zeolite} + \textit{Sodium salt}\\
Na_2O.Al_2O_3.2SiO_2 + CaCO_3 &= CaO.Al_2O_3.2SiO_2 + Na_2CO_3\\
Na_2O.Al_2O_3.2SiO_2 + CaSO_4 &= CaO.Al_2O_3.2SiO_2 + Na_2SO_4\\
Na_2O.Al_2O_3.2SiO_2 + Ca(NO_3)_2 &= CaO.Al_2O_3.2SiO_2 + 2NaNO_3\\
Na_2O.Al_2O_3.2SiO_2 + CaCl_2 &= CaO.Al_2O_3.2SiO_2 + 2NaCl.
\end{aligned}$$

Similar reactions take place when magnesiums salts form the second half of the equation instead of lime salts

When, in the filter, the sodium of the zeolite is sufficiently exhausted, it may be regenerated by running in an 8 per cent. solution of common salt, and allowing it to stand for about 8 hours when the following reaction is completed and the filter is again ready for use.

$$\textit{Calcium zeolite} + \textit{Common salt} = \textit{Sodium zeolite} + \textit{Calcium chloride}$$

$$CaO.Al_2O_3.2SiO_2 + 2NaCl = Na_2O.Al_2O_3.2SiO_2 + CaCl_2$$

The analyses in Table LIV include a group of alkali lakes from Western North America, and two analogous ones from Europe.

Comments on the Analysis

Soda Lakes, Nevada (Fig. 81).—The soda lakes near Ragtown, Nevada, lie in two circular depressions which are evidently craters of extinct volcanoes. The larger lake is 268.5 acres in area and the smaller is a pond of variable size.

The rim of the larger lake in its highest part rises 80 feet above the surrounding desert, and is 165 feet higher than the surface of the lake. The greatest depth of the lake is 147 feet, making a total depth for the depression of 312 feet, while the bottom is 232 feet lower than the general surface of the desert nearby. The walls of the crater show stratified beds of lapilli mingled with angular fragments of basalt up to 2 and 3 feet in diameter. Marly lake beds with fresh water shells and dendritic tufa are interstratified with the lapilli. The volcano was thus active both before and after the dendritic stage of Lake Lahonton.

TABLE LIV.—ANALYSES OF ALKALINE LAKE WATERS

	A	*B*	*C* Mono Lake, Cal.	*D* Owen's River	*E*	*F*	*G*	*H* Good-enough Lake	*I* Laacher See, Germany	*J* Palik Lake, Hungary	*K* Natron Lake near Thebes, Egypt
	Soda Lake, Nev.				Owen's Lake, Cal.						
	Surface	30.5 m. below				1905					
Cl	36.51	35.38	23.34	9.49	25.67	24.82	25.40	7.64	4.99	15.68	26.00
SO_4	10.36	10.50	12.86	15.53	9.25	9.93	9.89	7.08	2.97	2.92	
CO_3	13.78	15.89	23.42	29.84	32.51	24.55	22.70	41.41	50.97	41.02	32.90
PO_4	.....	.....	.....	.....	.....	0.11	.....	0.62			
B_4O_7	0.25	0.26	0.32	.....	0.48	0.14	1.89	Trace			
NO_3	.....	.....	.....	0.48	.....	0.45					
Li	.....	.....	.....	.....	.....	0.03					
Na	36.63	35.38	37.98	19.83	37.83	38.09	37.83	36.17	27.05	35.75	31.05
K	2.01	2.13	1.85		2.18	1.62	2.09	6.65			
Ca	.....	.....	0.04	8.92	0.02	0.02	....	0.02	9.90	0.66	3.57
Mg	0.22	0.21	0.10	3.45	0.01	0.01	....	0.04	2.77	3.35	3.62
SiO_2	0.24	0.25	0.14	12.37	0.29	0.14	0.20	0.04	1.35	0.27	1.36
Al_2O_3	.....	.....	Trace	.....	0.04	0.04	....	0.33	....	....	1.50
Fe_2O_3	.....	.....	Trace	0.09	0.02		....	....	....	0.35	
As_2O_3	.....	.....	.....	.....	.....	0.05					
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity permille	113.70	113.70	51.17	0.339	72.70	213.70	118.83	103.47	0.218	2.215	4.407

The lakes have neither effluent nor affluent, though some water may be supplied from subterranean sources. Russell thinks that the water is mainly supplied by percolation from Carson River, which is 50 feet above the lake level at the nearest point.

The trona deposited by the lake on the shore often contains casts of the larval cases of a fly which now lives in the lake in immense numbers.

The mineral matter of the waters of Soda Lake is regarded by Russell as "unquestionably derived from the springs that supply them and which has been dissolved from the lacustral beds and lapilli deposits through which their waters percolated during their subterranean passage" (p. 80). The lake contains nearly 428,000 tons of sodium carbonate and nearly four-fifths that quantity of sodium sulphate, and somewhat less than three times that amount of NaCl. The total mass of salts in the lake is in the neighborhood of two million tons. The lakes are worked for commercial purposes.

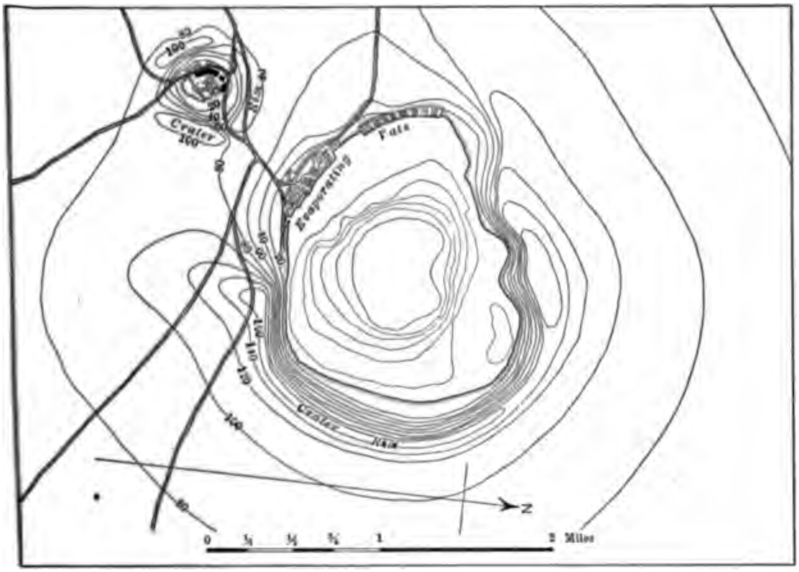

FIG. 81.—Contour map of Soda Lake, Nevada. (*After Russell. Monograph* 11, *U. S. G. S.*) Contour interval 20 feet.

It is probable that we have here an example of sodium carbonate waters formed by the exchange of bases between calcium carbonate and sodium zeolites in the basalts. The calcium carbonate may be contained in the percolating waters of Carson river, or it may be derived from the solution of the lime of the intercalated tufa deposits, or again it may be furnished by springs from deeper sources.

The following three analyses, of the deposits, from Big and Little Soda Lakes, are taken from Clarke.

TABLE LV.—ANALYSES OF SALTS FROM THE SODA LAKES, NEVADA

	A	*B*	*C*
	Big Soda Lake, 1868	Little Soda Lake, 1868	Market soda
Na_2CO_3	45.05	44.25	52.20
$NaH.CO_3$	34.66	34.90	25.05
Na_2SO_4	1.29	0.99	5.10
NaCl	1.61	1.10	3.31
SiO_2	.....	......	0.27
Insoluble	0.80	2.81	
H_2O	16.19	15.95	14.16
Total	99.60	100.00	100.09

Crystals of gaylussite ($CaCO_3$, Na_2CO_3. $5H_2O$) are also deposited from these waters. As will be seen from the analysis in columns *A* and *B* of the preceding table (Table LIV), no calcium is shown for the waters of this lake. This has been explained as due to the fact that the calcium brought in is used up as fast as supplied to form the gaylussite,[1] but may also be due to the exchange with sodium of the zeolites in its percolation as above noted.

The carbonates believed to exist in these and the waters of Owen's and Mono lakes are probably three in number.

Thermonatrite	$Na_2CO_3.H_2O$
Natron	$Na_2CO_3.10H_2O$
Trona (Urao)	$Na_2CO_3.NaHCO_3.2H_2O$

Mono Lake.—This is situated in Mono County, California and is a considerable body of inland drainage, lying at an elevation of 6,730 feet above sea level. The salinity of the water is greater than that of ocean water, being 51.17 permille or more, while the principal salts are sodium chloride, sodium carbonate, and sodium sulphate. Potash is also present, probably in the form of the chloride, of which it has been estimated that the waters contain approximately 10,000,000 tons.[1] A recent determination gives the amount of potassium chloride as 1.8342 grams per liter, the total salinity being 53.4724 grams per liter, *i.e.*, 53.47+ permille.[2] (For location see Fig. 92, p. 263.)

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[1] See T. M. Chatard, Bull. U. S. Geol. Surv. No. 60, 1890, p. 52, etc.

Owen's Lake (Fig. 92, p. 263).—This lies in western Inyo County, California, in a long and narrow valley between steep ranges, at an elevation of less than 4,000 feet above the sea. This elevation varies from year to year owing to fluctuation in precipitation. In February 1913 it was 3,577 feet, and the area of the lake was 97.2 square miles. The maximum depth at this time was 29.6 feet.[3] It receives the drainage of Owen's River, which heads in Mono County and flows between mountain ranges for more than a hundred miles. The entire valley has a length of 140 miles and a width varying from 20 to 40 miles. The lake has no outlet and like all bodies of water of this type is highly saline, the salinity being variable, as shown by the three analyses given. It was 213.7 permille in August, 1905. In October, 1876, it was 60.5 ‰; in May, 1912, 95.9 ‰; and in October, 1912 and February, 1914, it was 109.5 ‰. The salinity of Owen's River on the other hand, an analysis of which is given under *D* in Table LIV, is low, being at the point for which the analysis is given (Charlies Butte) 0.339 permille.

According to Phalen, the waters of Owen's Lake contain the following salts in grains per imperial gallon.

TABLE LVI.—SALTS OF OWEN'S LAKE

NaCl	2942.15 grains per imp. gal.
Na_2SO_4	956.80
Na_2CO_3	2914.43
K_2SO_4	35.74
K_2SiO_3	139.54
Organic matter	16.95

It is estimated that these waters contain 8,000,000 tons of potassium sulphate (Phalen), and further that if the waters were entirely evaporated a mass of anhydrous salts would remain, covering an area of about 25 square miles and having a thickness in the deepest part of the basin of 5 or 6 feet. This extent and thickness would be nearly doubled when the mother liquor and water of crystallization, which would remain under natural processes of desiccation, are considered.[1]

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[1] Elliott Mitchell, Nat. Geogr. Mag., Vol. XXII, No. 4, 1911.

[2] Phalen, W. C., Min. Resources of the U. S. for 1910, Pt. II, pp. 747-767.

[3] Gale, Bull. U. S. Geol. Surv. 580, p. 253.

Studies by Chatard on the fractional crystallization of the waters of Owen's Lake, where sodium carbonate is likewise manufactured for commercial purposes, gave the following results for the salts obtained. The waters of the lake are given in the first column, with a salinity of 77.098 ‰. The first crop of crystals was obtained when the water had been concentrated to one-fifth its original volume.

The first crop thus consisted chiefly of trona ($Na_2CO_3.NaHCO_3.2H_2O$). In the succeeding three crops, *C, D, E,* the carbonates diminish but the normal carbonate $Na_2CO_3.H_2O$ is greatly in excess, while the chlorides increase. The second and third crops deposited mostly sodium sulphate, and the fourth mostly sodium chloride. The last crop was obtained by chilling

TABLE LVII.—RESULTS OF FRACTIONAL CRYSTALLIZATION OF THE WATERS OF OWEN'S LAKE (CHATARD)

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
	Natural waters, Owen's Lake, sp. gr. 1.062 25°	1st crop crystals, sp. gr. of mother liquor 1.312 27.9°	2d crop sp. gr. of mother liquor 1.312 25°	3d crop sp. gr. of mother liquor 1.315 26.25°	4th crop sp. gr. of mother liquor 1.327 35.75°	5th crop sp. gr. of mother liquor 1.300 13.9°	Trona from Owen's Lake	Theoretical composition of trona
H_2O	......	14.51	4.33	3.43	2.24	11.03	16.16	15.93
Na_2CO_3	34.95	43.75	22.84	18.19	12.51	55.04	45.86	46.90
$NaHCO_3$	7.40	30.12	10.53	4.06	3.88	4.09	36.46	37.17
Na_2SO_4	14.38	3.18	25.44	26.70	19.01	5.70	1.25	
$NaCl$	38.16	7.44	35.06	45.59	60.99	19.16	0.32	
$Na_2B_4O_7$	0.63							
$NaBO_2$						2.01		
KCl	4.07	1.07	1.12	1.14	1.21	2.93		
$CO_3(CaMg)$	0.08	0.14						
$O_3(AlFe_2)$	0.05	0.01			0.01	0.02		
SiO_2	0.28	0.055	0.09	0.06	0.05	0.16		
Organic matter	......	0.032						
Insoluble	......	0.078	......	......	......	......	0.02	
	100.00	100.385	99.41	99.17	99.90	100.14	100.07	100.00

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[1] Gale, *loc. cit.*, p. 260.

the solution, and deposited chiefly sodium carbonate, with some chloride and less sulphate. Thus the order of deposition is (1) Trona, (2) Sodium Sulphate, (3) Sodium Chloride, and finally (4) (ignoring the minor constituents) the very soluble normal carbonate.

The rocks from which the salts were originally derived seem to have been mainly rhyolites, andesites, and other varieties rich in alkalies and relatively poor in lime. This is indicated by the fact that more calcareous sediments and gypsum were not formed, with the corresponding reduction of the alkaline carbonates.

The seepage waters from springs near Owen's Lake percolate through beds of volcanic ash and contain even a higher proportion of alkaline carbonates than the lake itself, as shown by the analyses.[1]

Artemia salina (Fig. 82) the alkali or salt-shrimp, occurs in abundance in these waters, and when these die in the concentrated water, they give it a reddish appearance.

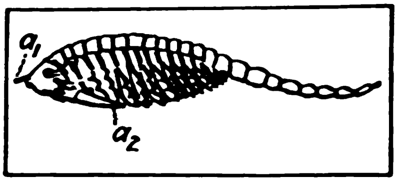

FIG. 82.—*Artemia salina*, the brine shrimp. (*After Leunis Synopsis der Thierkunde.*) Enlarged: a_1 = first, a_2 = second feeler.

From his study of the natural soda deposits, Chatard concludes that, "Natural soda is formed partly by direct decomposition of rocks through the action of air and water, aided at times by heat and pressure, and partly by subsequent decompositions occurring either in soils or in closed basins. These reactions, especially those of the latter class, are much influenced by the action of organic matter, which not only reduces sulphates, but also, in the form of certain organic acids, has been found to be a powerful reagent in rock decomposition."[2] The influence of zeolites in the volcanic rocks, on the formation of sodium carbonate as above outlined must also be taken into consideration.

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[1] T. M. Chatard. Natural Soda: Its Occurrence and Utilization, Bull. U. S. G. S. No. 60. 1890. pp. 27-101 ('94).

[2] Chatard, *loc. cit.*, p. 99.

Goodenough Lake.—This is a shallow pond 28 miles north of Clinton, British Columbia. Its waters are essentially a solution of sodium carbonate, and its concentration is high, the salinity of the sample analyzed being 103.47 permille. Like all such water bodies in arid or semi-arid regions, the salinity varies greatly from season to season, and during different years. From these waters, natron ($Na_2CO_3.10H_2O$) is deposited.

The Laacher See.—This celebrated lake in northwest Germany is the largest of a group of crater lakes or Maare, of which a number are scattered over the Tertiary volcanic territory of the Eifel. They represent explosive craters torn through the Devonic limestone and other formations of the region. Their form is nearly circular and they are commonly surrounded by walls of trachyte tuffs in which are bombs and fragments of the underlying basement rock. Extensive beds of lapilli have accumulated in the vicinty of the Laacher See and it is from the decomposition products of these volcanic rocks and the trachyte tuffs that the alkali of the water is derived. Owing to the fact that this lake, though without outlet lies in a region of humid climate, the salinity is very low, being only a little over 0.2 permille, a salinity which just takes it out of the category of fresh water bodies. It yields sodium carbonate on evaporation.

Soda Deposits of Hungary.—In Hungary, natural soda is found in many places, one of the most important deposits being near the town of Szegedin. It occurs as an efflorescence on the surface of moist places forming snow white crusts which often extend for miles. The crude soda is called "szekso" and is collected by scraping the surface. The chief substance of this efflorescence are sodium carbonate and sodium chloride with sodium sulphate and calcium sulphate next. By natural leaching soda lakes are produced of which Palic Lake is an example (see Analysis *J*, Table LIV, p. 236).

Natron Lakes of Egypt (Figs. 83–85).—These lakes are situated in Wadi Natron in Lower Egypt, southwest of the delta (see Fig. 54, p. 120). The wadi is a graben-like depression, with a floor nearly twenty kilometers in length, and ranging from zero to 23 meters below the level of the Mediterranean. The deepest portion of the valley lies near the northern fault-scarp, which rises about 75 meters above the valley floor, and in this portion of the valley lies the chain of Natron lakes, of which there are 11 large, and 7 or 8 smaller ones. In these lakes sodium carbonate and sulphate is deposited. The valley floor ranges in width up to 10 kilometers, but is usually much narrower. At the convent of Baramus the southern rim of the valley rises about 80 meters above its floor, which is here approximately at sea-level. At the convent of Makarius, however, the elevation of this ridge is nearly 200 meters. The nearest Natron Lake is about 40 kilometers from the Rosetta arm of the Nile, the character of the country between these points being shown in the cross-section Fig. 84, which is, however, much exaggerated in vertical scale.

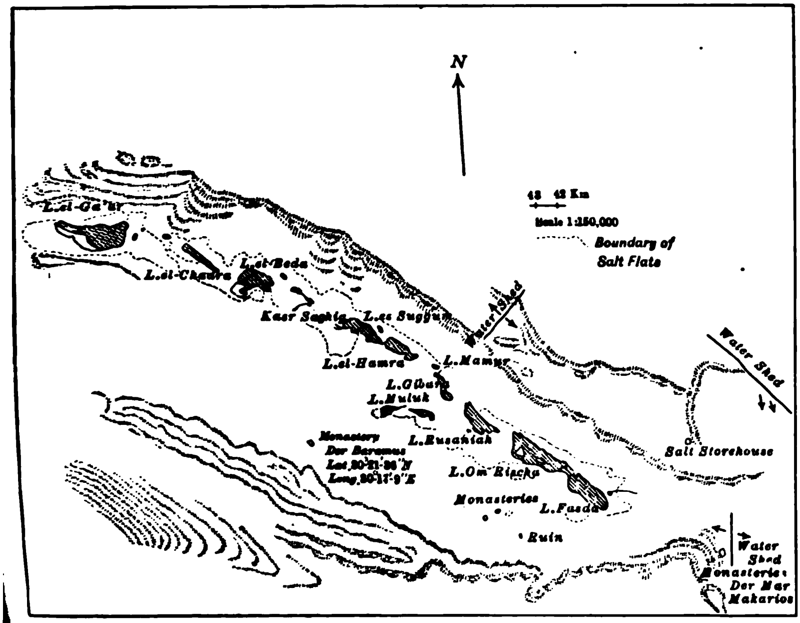

Fig. 83.—Map of the Natron Lakes of Egypt. (*After Schweinfurth—Zeitschrift der Gesellschaft für Erdkunde Berlin*, Vol. 33, pl. 1, 1898.) For location see map, Fig. 54, p. 120.

The waters of the Natron lakes have their highest stand toward the end of December, when the depth in some is two meters, though the average is only 70 centimeters. During May, June and July, when the Nile has its hundred days of low water, most of the Natron lakes dry up, the evaporation being here from 20 to 25 mm. per day. Only lakes Ga'ar and Rusaniah retain some water. Many springs occur in the neighboring flats, some saline, but many nearly fresh, and marked by dense growths of reeds (*Phragmites communis* L. and *Typha* *latifolia* L.). The springs as well as the lakes themselves evidently derive their water from the Nile this being indicated by the harmonious seasonal fluctuation in the waters. All of the lakes carry natron as well as common salt, except lake Om Rischa, which carries only sodium chloride and no natron.

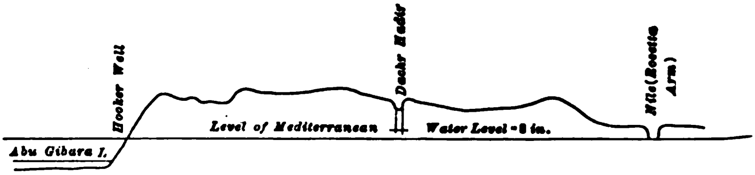

FIG. 84.—Section from the Nile (Rosetta Arm) to the Natron Valley at Abu-Gibara. (*After Schweinfurth.*)

The salt which separates at the bottom of the lakes has the following composition:

TABLE LVIII.—ANALYSES OF SALTS FROM THE NATRON LAKES, EGYPT

	A. Laugier	Berthollet	Lewin
Sodium carbonate	22.44	23.0	18.44
Sodium sulphate (Glauber salt)	18.35	11.0	11.4
Sodium chloride	38.64	52.0	62.0
Calcium carbonate	.....	0.9	
Impurities and water	20.00	12.9[1]	
Total	93.43	99.8	91.84

[1] Sand, 3 per cent.; iron oxide, 0.2 per cent.; water, 9.7 per cent.

The differences in the analyses are partly due to the fact, that the samples were obtained from different deposits, and partly because they were obtained at different times. The analysis by Berthollet is one of the earliest and that by Lewin among the latest. So far as the sodium carbonate and sulphate are concerned, the changes have been very slight during this interval.

In some of the lakes, both natron and common salt separate out. They form distinct layers, the chloride salt occurring in beds 10 inches thick, and the carbonate salt in 27-inch or heavier beds. The lakes are generally surrounded by a belt characterized by the efflorescence of pure sodium carbonate. The water which feeds these lakes is, as stated above, believed to filter in from the Nile, passing through limestones, and gypsum-, and rock-salt-bearing deposits. The water passing through these beds becomes charged with sodium sulphate, which according to Sickenberger[1] is changed to the carbonate by the influence of algæ, bacteria and other microörganisms which live in the springs and the lakes and which are so abundant, that they give the well-known red color to the lakes. Others, however, consider the sodium carbonate as due to the double decomposition of sodium sulphate with the bicarbonate of lime. The sodium sulphate is formed by reaction between sodium chloride and calcium sulphate.[2]

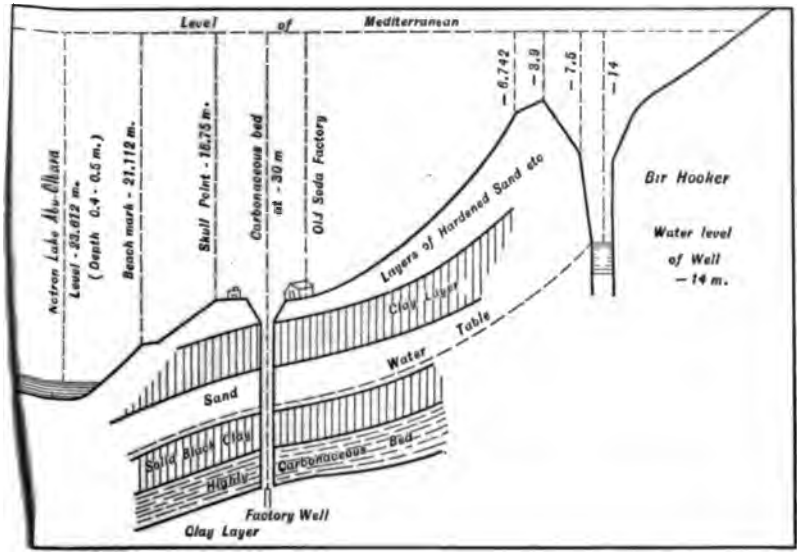

FIG. 85.—Geological section of a portion of Wadi Natron at Lake Gibara. (*After Schweinfurth.*)

The carbonization of the sodium sulphate has also been regarded as brought about by contact of the waters with a carbonaceous shale, which has been found at a depth of about 10 meters, and below a heavy bed of black clay (Hooker well, see section, Fig. 84). The geological structure at this point is indicated in the larger section, Fig. 85.

The marked differences of opinion regarding the origin of the

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[1] Wasserquellen der Sahara. Zeitschrift für praktische Geologie, 1894, p. 263. Chemische Zeitung, 1892, pp. 1645, 1691.

[2] G. Schweinfurth and L. Lewin, Beiträge zur Topographie und Geochemie des aegyptischen Natron-Thales. Zeitschrift der Gesellschaft für Erdkunde, Berlin, Vol. 33, pp. 1-24, pl. 1, 1898.

[illegible] mingled with the other salts. Borax occurs in three forms: [illegible] crust from one to three inches thick, more or less mixed with earth; (2) as *tincal*, in crystals in the mud below the [illegible] *ulexite* or borate of soda and lime. This occurs in a [illegible] area around the salt, in the "cotton ball" form embedded in [illegible] wet, stiff clay.

The sulphate of soda occurs as a solid, white, ice-like layer a [illegible] distance below the surface and close to the central salt [illegible] surrounding it except on the west. It has a considerable thickness. Carbonate of soda has also been found in one [illegible]. The borax is apparently derived from springs, some of [illegible] occur in the playa.

The following analyses of crude borax from this marsh are [illegible]: *a*, from the southeastern part of the playa, [illegible] an area of about 40 acres and from 1 to 5 inches thick, [illegible] of the preceding, from an area of 100 acres and 2 [illegible].

[illegible] from the vicinity of the salt bed, and *d* represents [illegible] crust from 2 to 6 inches thick which overlies a [illegible] deposit of borate of lime.

[illegible] Analyses of Borax from Rhodes Marsh, Nevada

	a	*b*	*c*	*d*
[illegible]	40.06	57.20	14.6	15.03
[illegible]	1.16	5.80		
[illegible]	[illegible]6.00	10.70	30.5	20.10
[illegible]	5.00	......	Trace	8.07
[illegible]	8.07	9.00	26.6	15.90
[illegible]	[illegible]8.71	17.30	38.3	40.88
	100.00	100.00	100.00	100.00

[illegible] This lies about 16 miles northwest from Colum[illegible] one of the most productive borax fields [illegible]. Like others, it is a dry playa with a soft, [illegible] a deposit of crude borax. It covers [illegible] by 5 or 6 in length. Its thickness varies [illegible] inches (map, Fig. 92).

[illegible] a small basin situated about 25 miles [illegible]. It is, like the others, a playa in which crude

$3Al_2O_3.4SO_3.6H_2O$) and alunogen ($Al_2(SO_4)_3.18H_2O$). Halotrichite ($FeSO_4Al_2(SO_4)_3.24H_2O$) is another alum species found sometimes in considerable abundance.

CONCENTRATION OF SALTS BY PLANT GROWTH

Bacteria and Seaweeds.—We have seen in earlier sections that many seaweeds are active in separating salts from the medium in which they live. The nullipores precipitate lime and magnesia salts in and upon their tissues, and the same lime-secreting function is performed by the fresh water stone-wort or Chara, also a member of the tribe of algæ. Minute members of this lowly group of plants are believed to be responsible for the formation of oolite deposits, and as we shall see presently, some of the lowliest of plants, the bacteria, are actively engaged in the fixation of atmospheric nitrogen as well as in the oxidation of ammonium and other products of organic activity into nitrates and nitrites. Finally, we have seen that some of the larger seaweeds or kelps separate both potash and iodine from sea water and that this may be obtained again from their ash after incineration, or is liberated upon the decay of the plant.

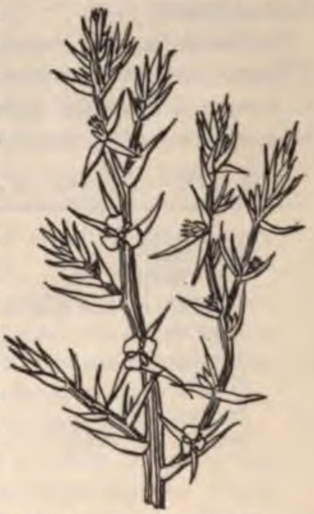

FIG. 86.—Salsola kali. (*Drawn by Mary Welleck.*)

Soda-secreting Plants.—Plants of higher types, whose habitat is primarily terrestrial, are also engaged in the separation of salts of various kinds from the soil upon which they grow, while at the same time they take the carbonic acid gas and nitrogen from the atmosphere to build their tissues. Secretion of salts is probably a function of all terrestrial plants, but some perform this absorption of salts more rapidly and to a greater amount than others. Attention has already been called to the soda plants of the Mediterranean coasts and the Canary Islands, which in old days were the main source of sodium carbonate. One of these plants, the Saltwort or *Salsola kali* of botanists (Fig. 86), the *alkali* of the Arabians,[1] cultivated especially on the Spanish coast, carries from 14 to 20 per cent. of carbonate of soda in its ash, and was a source of this salt even in the 19th century. Another, the *Mesembryanthemum crystallium* or ice plant of the Canary Islands coasts was likewise an important source of this salt in the past. Both of these obtain the sodium from the salt-impregnated flats along the sea coast where they grow. The common saltwort or kelpwort, which is a member of the Goosefoot family or *Chenopodiaceæ*, is widespread on sea beaches, not only in Europe and Western Asia but occurs also in North and South America and in Australia. It is also found sparingly inland in the United States.

In the Salinas of Argentina this plant is known as the Jume (Chume) and it is characteristic of the Argentine salt steppes. It is burned while still green. The ash of the entire plant (leaf, bark and wood) contains the following constituents (Napp).

TABLE LIX.—ANALYSIS OF ASH OF ARGENTINE JUME OR SALTWORT

	Per cent.
Iron oxide	0 64
Salt (NaCl)	19.38
Sulphate of lime ($CaSo_4$)	0.50
$Mg.CO_3$	0.94
Potassium phosphate	21.15[2]
K_2CO_3	7.80
Sodium silicate	7.86
Sodium carbonate	41.73
	100.00

This shrub is richer in ash than any other known plant and burns while still green, producing an intense heat.

This ash is largely used in Argentine for the manufacture of soap.

Another soda-secreting plant is the glasswort or marsh-samphire of the genus *Salicornia*, a succulent saline plant of the same family, with leafless jointed stems, which store a large proportion of soda. This also was formerly used for making soda ash or *barilla* for the manufacture of glass and soap. The genus has

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[1] Arabic *Al*, *the* and *qualiy*, ashes of Saltwort; *qualay*, to roast in a pan, fry.

[2] Reported as 12.15, which according to Von Buschmann (II, p. 434) is probably an error of transposition.

8 species, all native of marshes or saline soils throughout the world, three of them occurring on the Atlantic and Pacific coasts of North America, and one in the alkaline places of the interior.

Sodium is also taken by salt plants from the soil where it originated from the decomposition of soda minerals of igneous rocks. This may occur in regions far removd from the sea. One of the best known examples is that of the salt plants growing on the steppes and upon the plains of the Araxes in Armenia. Where the soil is rich in sodium sulphate, that salt is taken up by the plants; but where the principal salt in the soil is sodium chloride this is converted into carbonate and as such stored by the plants in their tissues. By the growth and decay of these plants, an annual enrichment of the upper layers of the soil in these concentrated salts is effected, and the leaching of this soil and the further concentration of the leachings in basins, where waters are constantly subject to evaporation, results in the formation of salt lakes with very strong brines. The common tamarisk, *Tamarix gallica*, a native of the Mediterranean region and southern Asia, is an example of a salt-secreting shrub or small tree, which grows in salty as well as other ground. Its stem and leaves contain much sulphate of soda. Another species, the Indian salt tree, *Tamarix orientalis* has its twigs frequently covered with a slight efflorescence of salt which is used by the poorer natives.

In the interior of Brazil, salt is made from the ashes of the Takoara and Aguape, plants which grow in stagnant water.

Potash-secreting Plants.—That potash is taken from the soil by many woody plants is a matter of common knowledge. Until recently, and to some extent even now, the manufacture of potash-lye by the leaching of wood ashes was carried on in many a rural household. In 1913 the only potash known to have been produced in the United States was made from wood ashes, but in 1916, although the production from this source amounted to 412 short tons of available K_2O valued at $270,000.00, this was less than 4¼ per cent. of the total potash production in the United States. In 1917 a total of 1,035 tons of crude potash was produced in the United States from wood ashes estimated to contain 621 tons of pure potash (K_2O) and valued at $549,150.00 or about $884.00 a ton of pure potash (K_2O). (Min. Res. U. S., 1917, part 12, p. 454.)

The amount of mineral matter which remains after burning or decay of the plant as "ash," varies in general from 0.143 up to

TABLE LX.—ANALYSES OF GRASSES, LEAVES, ETC.

	Grasses			Straw					Autumn leaves			Air dried wood		
	Meadow grass	Rye grass	Timothy grass	Heather straw	Broom straw	Fern straw	Reed straw	Sedge straw	Beech leaves	Oak leaves	Scotch fir leaves	Beech-wood (trunk)	Oak (wood)	Scotch fir (wood)
Water	70.00	70.00	70.00	20.00	16.00	16.00	18.00	14.00	55.00	60.00	55.00	15.00	15.00	15.00
Ash	2.33	2.13	2.10	3.61	4.89	5.89	3.85	6.95	3.05	1.96	0.63	0.55	0.51	0.26
K_2O	0.60	0.53	0.61	0.48	0.69	2.52	0.33	2.31	0.16	0.07	0.06	0.09	0.05	0.03
Na_2O	0.16	0.09	0.06	0.19	0.05	0.27	0.07	0.51	0.02	0.01	.....	0.02	0.02	0.01
Mg.O	0.11	0.05	0.08	0.30	0.28	0.45	0.05	0.29	0.18	0.08	0.06	0.06	0.02	0.02
CaO	0.27	0.16	0.20	0.68	0.32	0.83	0.23	0.37	1.37	0.95	0.26	0.31	0.37	0.13
P_2O_5	0.15	0.17	0.23	0.18	0.16	0.57	0.08	0.47	0.13	0.16	0.13	0.03	0.03	0.02
SO_3	0.12	0.08	0.08	0.16	0.07	0.30	0.11	0.23	0.11	0.09	0.03	0.01	0.01	0.01
SiO_2	0.69	0.84	0.75	1.27	0.19	0.36	2.75	2.18	1.03	0.61	0.08	0.03	0.01	0.04
Cl	0.19	0.11	0.11	0.08	0.05	0.60	.....	0.39	0.01	.....	0.03			
S	0.06	0.07	0.08											

2 per cent., but may in case of hay reach 5 to 9 per cent., and in the white sage nearly 12 per cent. of the plant. This ash contains from 3 to 34 per cent. of potash, according to the type of the plant, the average in the case of trees being 5 per cent. The soda content ranges from 2.75 to 16 per cent., often exceeding that of the potash, as in the pine (*Pinus sylvestris*), where it is about six times that of the potash. In grasses, on the other hand, potash is a more important constituent than soda. In table LX, p. 250, analyses of grasses and other plants are given. Analyses of "Canada Hardwood Ashes" made by the Connecticut Experiment Station between 1903 and 1917 show a range from 2.77 to 4.74 per cent. water-soluble potash, from 1.15 to 1.42 per cent. phosphoric acid and from 23.8 to 30 per cent. lime.[1] The ashes have steadily decreased in quality and value since 1900. Analyses of household wood ashes of Connecticut averaged 5.99 per cent. water-soluble potash, 2.68 per cent. phosphoric acid and 33.58 per cent. lime, the extremes of potash being 2.93 and 7.51 per cent. The difference is due to variation in ash content of the wood and partly to the heat of burning; great and continued heat causing some potash to combine with the impurities present (sand or earth) and to become insoluble.

"A bushel of dry ashes from the stove or fireplace weighs about 48 pounds and may contain about 2.9 pounds of potash, 1.25 pounds of phosphoric acid and 16 pounds of lime. . . . .

"Seventeen hundred pounds, or about 35.5 bushels contain as much soluble potash (50 pounds) as 100 pounds of muriate of potash and in more desirable form, besides 45 pounds of phosphoric acid and 570 pounds of lime, in form of fine carbonate. No better fertilizer for clover or [for] legumes can be suggested."[2]

The following table from Jenkins shows the percentages of potash and phosphoric acid from the ashes of common fruit and vegetable wastes.

The ashes of corn cobs have been found to contain as much as 21.13 per cent. water-soluble potash and 4.01 per cent. phosphoric acid.

Ashes of blackberry canes have furnished as high as 10.3 per cent. of potash, those of gooseberries 13 per cent. and those of raspberries 7.9 per cent.

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[1] E. H. Jenkins, Bull. 198 Connecticut Agricultural Experiment Station, November, 1917, page 47.

[2] Jenkins, *loc. cit.*, p. 48.

TABLE LXI.—POTASH AND PHOSPHORIC ACID CONTENT OF ASH OF FRUIT AND VEGETABLE WASTE, ETC. (JENKINS)

	Potash	Phosphoric acid
Apple parings	11.74	3.08
Banana stalks, yellow	49.40	2.34
Banana stalks, red	46.64	3.04
Banana skins	41.76	3.25
Grape-fruit skins	30.64	3.58
Lemon skins	31.00	6.30
Orange skins	27.04	2.90
Peanut shells	6.45	1.23
Potato peelings	27.54	5.18
Corn cobs	17.25	3.14
Cigar ashes	16.81	2.57

The percentage of K_2O in sugar beets ranges from 0.269 to 0.320 and that of P_2O_5 from 0.023 to 0.121 of the total, depending on the locality, condition of soil, etc.

Hay made from salt marsh grasses and river meadow grasses have furnished the following plant foods where used as fertilizers.

TABLE LXII.—PLANT FOODS IN HAY OF SALT MARSH AND RIVER MEADOW GRASSES (JENKINS)

	Pounds per ton of hay		
	Nitrogen	Phosphoric acid	Potash
Salt Marsh Grasses: (Figs. 87–89)			
Black grass (*Juncus gerardi*)	23.8	5.0	42.0
Salt grass (*Spartina juncea*)	17.4	5.4	14.0
Three square (*Scirpus americanus*)	23.8	5.0	30.2
Creek sedge (*Spartina glabra*)	21.8	7.4	21.2
River Meadow Grasses:			
Black bent (*Panicum virgatum*)	29.0	7.0	10.0
Blue bent (*Andropogon provincialis*)	21.0	6.0	11.0
Indian grass (*Sorghastrum nutans*)	20.0	10.0	19.0
Poverty grass (*Andropogon scaparius*)	11.0	5.0	11.0

Analyses of the ashes of witch-hazel or black birch have furnished from 4.47 to 4.61 per cent. water-soluble potash (or a total of 5.09 per cent. potash); 4.52 to 4.95 per cent. phosphoric acid; 37.75 per cent. of lime and 4.68 per cent. of magnesia.

Analyses of the Tule or fresh water swamp sedge (*Scirpus lacustris* var. *occidentalis*) gave 45.3 per cent. of water-soluble salts in its ash, these comprising Na_2O, 8 per cent.; K_2O, 16.8 per cent.; Cl, 14.4 per cent.; SO_3, 4.7 per cent.; CO_2, 1.4 per cent. Besides this there is 40.3 per cent. of water-insoluble mineral matter (sand, clay, iron oxide, etc.) and 14.4 per cent. unburned carbon.[1]

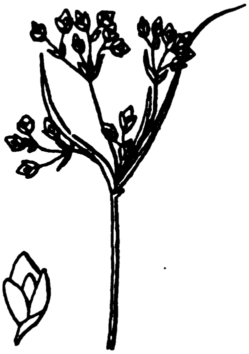

Fig. 87.—Juncus gerardi.

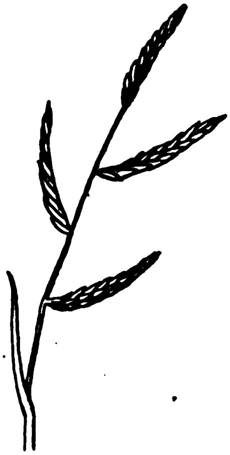

Fig. 88.—Spartina juncea.

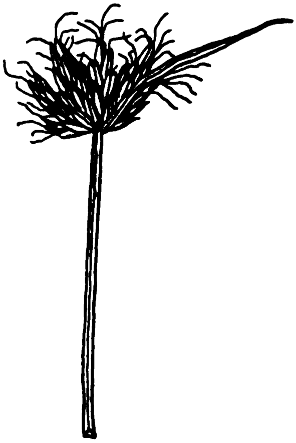

Fig. 89.—Scirpus americanus.

(*From Drawings by Mary Welleck*).

Sage brush and other plants of the interior semi-arid regions and alkali lands of the United States (Utah) have furnished the following analyses.[2]

Table LXIII.—Analyses of Sage Brush, etc. (Hirst and Carter)

	Percentage of dry matter	Percentage of ash	Percentage of potassium (K) in ash	Potassium in dry plant calcul.
Sage brush (*Artemisia tridentata*)	75.66	10.47	4.10 to 5.42	0.43
White sage (*Artemisia trifida*)	61.08	11.89	13.77	1.64
Rabbit brush (*Chrysotomus greenier*)	83.31	5.78	13.04	0.75
Brigham tea (*Ephedra trifurca*)	89.56	5.84	5.94	0.35
Greasewood (*Sarcobatus vermiculatus*)	79.03	7.63	12.61	0.96

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[1] P. L. Hibbard, Agricultural Experiment Station, College of Agriculture, Berkeley, Calif., Bull. No. 288, Nov., 1917, p. 189.

[2] C. T. Hirst and E. G. Carter, Utah Agricultural College Experiment Station Circular No. 22, pp. 8–11.

In the following table the ash content and the amount of K_2O in it is given for a number of common hard-wood and soft-wood trees.*

TABLE LXIII*a*.—ANALYSES OF WOOD ASHES

Species	Ash content of dry wood, per cent.	Potash in ash (K_2O) per cent.
Hardwoods:		
Hickory	0.81	18.93
Red Oak	0.94	16.41
White Oak	0.41	29.90
Post Oak	1.21	15.46
Dogwood	1.05	20.03
Ash	0.47	34.74
Chestnut	0.20	13.33
Sycamore	1.10	18.24
Magnolia	0.67	19.54
Average for hard woods	0.76	20.28
Softwoods:		
Pinus palustris	0.54	15.35
Pinus mitis	0.38	12.97
Picea nigra	0.32	10.43
Average for soft woods	0.41	12.91

Salts from African Plants.—Several types of plants are used for the manufacture of salt or salt substitute in the interior of Africa, especially in the southern Soudan. These include grasses, reeds and other plants, even trees. On the borders of Lake Chad (Tsada) the roots of the caper-bush (*Capparis spinosa*) (?) are dug and burned and the ashes leached for salt. Other plants thus treated in various parts of Africa are the Durra or Guinea corn (*Sorghum vulgare*) and other tall grasses and reeds, various labiate and other flowering plants and shrubs, the Siwak or tooth-brush tree (*Sal-*

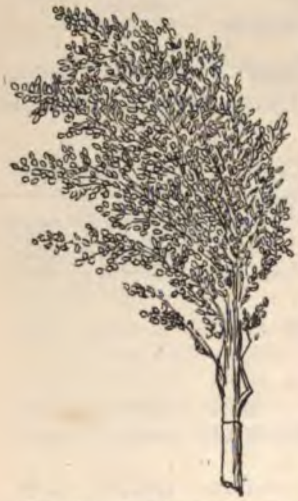

FIG. 90.—Sorghum vulgare. (*Drawn by Mary Welleck*).

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* Earnest Bateman, Chemical and Metallurgical Engineering, Nov. 12–19, 1919, p. 616.

vadorea persica),[1] the Suak tree, the Deleb palm or Palmyra (*Borassus flabellifer*), the banana, etc. Salt is leached from the ashes of a linden-like tree or shrub *Grewia mollis* in eastern Equatorial Africa (Gazelle River district). In the Congo region, salt is made from the common and widespread "Tropical duckweed" (water lettuce of the West Indies), *Pistia stratiotes*, a floating plant filling streams and ponds with a rosette of pale pea-green rounded and downy leaves. This is dried by exposure in the sun, and burned, after which the ash is placed in pots with finely perforated bottoms, and covered with water. The product of the leaching is gathered in shallow basins and evaporated over a fire. The result is a dark gray substance which has a saltpeter taste and has to be leached again for the salts required. An analysis of the saline product of Pistia and other plants produced by the negroes of the Ubangi district gave the following composition.

TABLE LXIV.—COMPOSITION OF SALT-SUBSTITUTE MADE FROM AFRICAN PLANTS (PISTIA, ETC.)

Potassium chloride	67.98
Potassium sulphate	28.73
Potassium carbonate	1.17
Insoluble	1.65

It is remarkable that there is here no trace of sodium chloride, while the potassium carbonate, which generally forms a considerable proportion of the ash of plants is very low. The natives have learned to select the plants low in this salt, which, because of its caustic character, makes the product unfit for consumption.

The grasses of the many islands in the Congo River also furnish an ash from which a salt-substitute is obtained.

LAKES AND PLAYAS THE ALKALINE AND SALINE CONTENT OF WHICH ARE CHIEFLY DERIVED FROM LEACHING OF WOOD ASHES

Soda Lakes of Armenia.[2]—On the plains of the Araxes in Armenia are many lakes in which sodium carbonate as well as chloride and sulphate occur. They are situated in the volcanic region of Mt. Ararat and derive their salts from the decomposition of the volcanic rocks. Lake Tasch Barum (Tashburun) carries 66.6 permille of salts, mainly NaCl (Analysis *A*, Table LXV). In hot weather, crusts of salt of a reddish color and up to a half inch in thickness are deposited on its shores. Of these an analysis is given in column *B* of the Table LXV. Red Lake, so named on account of the color of its water, lies on the left side of a valley close under the steep declivities of the greatest height of the Gundusdag range, which is composed of sandstone, dolomite, slate, and limestone, injected by red quartz-porphyry. The surface of the country is formed of a whitish clay which supports a strong growth of soda plants.

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[1] Probably the mustard of Luke, xiii, 19.

[2] Abich, Journ. für Prakt. Chemie, Vol. 38, p. 4, quoted by Chatard, Bull. U.S.G.S. 60, pp. 39–40.

Red Lake is about a mile in circumference and its shores are made of soft mud, covered with crusts of a hard reddish salt which has a laminated fracture. The crusts extend out upon the surface of the lake and portions are floating upon it, giving it the appearance of being about to freeze. This is largely sodium sulphate, as shown by Analysis *E*, Table LXV. The bottom is likewise covered by a crust of salt of similar character (Analysis *D*). The water (Analysis *C*) carries 306.3 permille of salts. The carbonates as well as the sulphates have crystallized out almost free from water, a circumstance attributed by Abich to the formation of a double salt of sodium sulphate and carbonate, which he calls "makite."

Other lakes and pools occur in this vicinity, the analysis of one with water of wine-yellow color and a salinity of 347.4 permille is given in Column *F*.

TABLE LXV.—ANALYSES OF WATER AND SALTS OF SODA LAKES OF ARMENIA

	A	*B*	*C*	*D*	*E*	*F*
	Tash Barum		Red Lake			Yellow Pool, water
	Water	Crusts	Water	Crusts		
				Bottom	Floating	
Na_2CO_3	14.71	22.91	12.08	18.42	16.09	68.90
Na_2SO_4	10.36	16.05	18.18	77.44	80.56	15.55
NaCl	74.61	51.49	69.73	1.92	1.62	15.50
H_2O	.....	9.88	.....	1.18	0.55	
Total	99.68	100.33	99.99	99.96	98.82	99.95

The sodium salts of this region are in part produced by the decomposition of the igneous rocks, but Abich holds that the chief accumulation is due to the growth and decay of the soda-secreting plants of that region. These yield an ash rich in soda-salts, those of Armenia being richer in Na_2CO_3 while those from the steppes are richer in Na_2SO_4. The soils of the steppes contain much Na_2SO_4, but little NaCl, which abounds in the soil of Armenia. From this, Abich concludes that the Na_2CO_3 of the plants is derived from the NaCl of the soil. The growth, death, and decomposition of these plants continually increases the amount of Na_2CO_3 in the soil from which it is leached out and concentrated in the lake waters.

The Alkali Lakes of Nebraska.—Another interesting group of examples of lakes the waters of which are rendered alkaline by the leaching of wood-ashes is seen in the alkali lakes of the Sand Hill district of Northwestern Nebraska[1] (Fig. 91).

These lakes lie in shallow depressions in a sand dune area now largely covered by vegetation. The depressions or "sinks" were apparently formed by wind erosion, and they receive the natural drainage of the region but have no outlets. They are shallow and readily filled by mechanical detritus carried in by wind and water, one of these, Watts Lake, having lost three-fourths of its area in this manner in ten years. In area these lakes vary up to several square miles, the deeper ones containing fresh water but the shallower ones being highly alkaline, the salinity ranging up to 135 permille or over.

The climate of the region is one of considerable annual variation. The temperature in winter is not infrequently as low as −20°F., while a temperature of 110°F. is occasionally reached in summer. The annual precipitation is from 15 to 18 inches, about 70 per cent. of this falling during the growing season. The annual evaporation is approximately 5 feet. The region was formerly covered with dense vegetation, among which pines formed the chief trees, while among the herbs Buffalo grass and bluegrass probably predominated, as indicated by the abundance of these grasses today. Before the advent of the white man the region was annually burnt over by the Indians. As a result the sand became mingled with an abundance of ash from which the alkalies were in part leached by the drainage and carried into the lakes, where the high evaporation brought

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[1] Victor Ziegler, The Potash deposits of the Sand Hill region of northwestern Nebraska. Colorado School of Mines Quarterly, Vol. 10, No. 3, 1915, pp. 6–26.

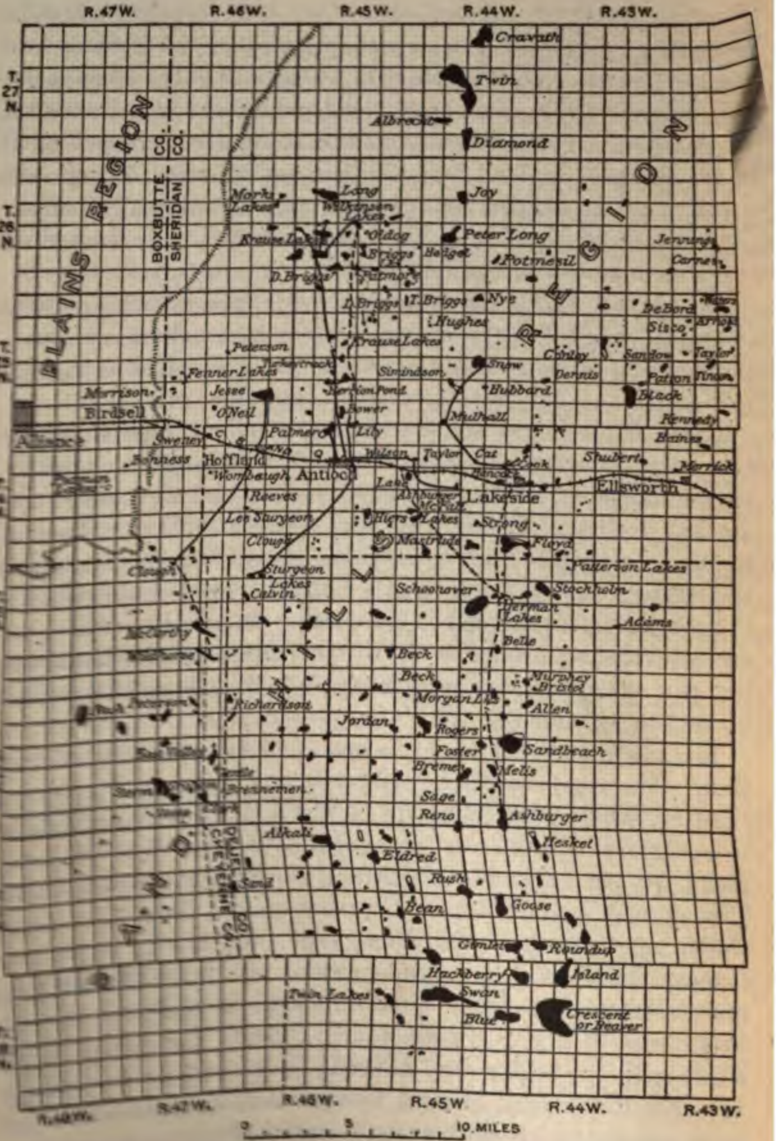

FIG. 91.—Map showing potash lake district in western Nebraska. (*Nebraska Conservation and Soil Survey.*)

about their concentration. In the following table are given a few of the analyses of the waters of some of these lakes, from which it appears that the potash and soda content is about the same, regardless of the salinity of the water. In the waters free from chlorides, the bicarbonate radical is highest, not falling below 8 per cent. and averaging 25 per cent. These waters are essentially carbonates and sulphates of potash and soda, with one or the other alkalies, usually the soda in excess. In another group of lakes the chlorides are high, the NaCl content ranging up to nearly 40 per cent.

TABLE LXVI.—ANALYSES OF WATERS OF ALKALI AND SALINE LAKES OF THE NEBRASKA SAND HILL REGION (J. H. LOW, QUOTED BY ZIEGLER)

Radicals	1	2	3	4	5	6	7	8	9	10
K_2O	22.48	10.88	8.96	19.98	28.36	14.50	18.78	26.82	25.00	3.93
Na_2O	24.89	26.87	45.01	11.05	27.49	38.94	20.05	21.64	20.20	37.56
CO_3	11.82	2.21	29.65	2.80	20.06	28.40	7.13	8.35	4.31	8.86
HCO_3	6.29	1.39	7.91	3.40	7.56	12.13	8.02	14.98	37.45	42.69
SO_4	25.01	38.88	2.05	23.56	12.03	0.44	22.74	23.38	9.31	5.74
NaCl	9.49	19.77	4.33*	39.20	3.97*	2.10*	23.22	3.66*	1.76*	0.71*
SO_2	......	......	2.07	......	0.52	3.49				

* Chlorine.

COMBINATION OF SALTS

	1	2	3	4	5	6	7	8	9	10
K_2SO_4	41.63	20.12	4.46	36.98	27.07	1.03	34.70	53.96	22.06	6.78
K_2CO_3	......	......	9.41	......	20.83	20.39	......	......	11.44	3.58
Na_2CO_3	28.51	5.33	64.29	6.75	32.37	52.45	17.20	21.71	5.06	20.52
$NaHCO_3$	9.97	2.20	12.59	5.43	11.99	19.14	12.82	16.28	56.98	67.47
NaCl	9.49	19.77	7.18	39.20	6.55	3.46	23.22	6.56	2.94	1.16
Na_2SO_4	10.39	52.53	......	11.68	......	......	12.06			
SO_2	......	......	2.07	......	0.52	3.49				
Total salts in permille	106.10	95.40	83.10	78.60	43.90	37.00	20.40	11.60	4.10	4.00

The muds from the lakes also show a high potash content, having been especially active in absorbing this salt. The following analyses of these muds are taken from Bull. 540, U.S.G.S., p. 466.

TABLE LXVII.—ANALYSES OF MUDS FROM NEBRASKA LAKES

No.	Source of sample	Soluble portion expressed as per cent. of sample	K_2O content expressed as per cent. of soluble portion
26	1 foot below surface of Jesse Lake, 40 feet from shore	9.35	25.42
77	1 foot below surface of flat one-fourth mile N. of R.R., 2 miles east of Reno postoffice	3.04	14.80
112	Lake at Lakeside	3.58	12.03
115	4 feet below surface of Jesse Lake	4.63	28.92
116	7 feet below surface of Jesse Lake	4.07	24.78
126	Lake in Sec. 1, T. 21 N, R. 46 W	3.47	13.20
	Average of 6 samples	4.69	19.86

In the next table, also from Bull. 540, p. 466, are given analyses of alkali crusts taken from partially or wholly dried up lake basins.

TABLE LXVIII.—ANALYSES OF ALKALINE CRUST FROM NEBRASKA LAKES

No.	Source of sample	Soluble portion expressed as per cent. of sample	K_2O content expressed as per cent. of soluble portion
25	Crust on southeast margin of Jesse Lake	34.06	21.00
75	Alkali from road 8 miles west of north of Lakeside	4.62	6.16
78	Alkali sand south of railroad, 3½ miles east of Reno postoffice	8.51	11.27
94	Surface incrustation east end of Crevath Lake	34.05	17.17
113	Surface incrustation south edge of pond 1 mile west of north of Lakeside	30.85	2.40
117	Surface incrustation Jesse Lake	20.25	17.39
132	East pond on Cluff place	8.97	29.70
134	Pond 1½ miles west of preceding	15.12	12.76
	Average of 8 samples	19.55	14.73

In 1916 these alkali lakes have produced the largest output of potash in the United States, they having "afforded the most readily available supply of moderately high-grade potash salts, which are obtained by direct drying of the raw material, with perhaps as few technical complications as could be involved in any chemical operation."[1] The production in 1917 was 61,053 short tons of crude potash containing 14,558 short tons of K_2O, about 45 per cent. of the total domestic product for the year.[2] The cost of producing potash in the alkali-region of Nebraska is between $20.00 and $44.00 a short ton, or an average of $30.00 a short ton of crude salts. This corresponds to an average of about $120.00 a ton of potash ($K_2O$), but the cost would be much reduced by improved labor and fuel conditions.[3]

It should here be noted that whereas the normal price of potash during the period of import before the war was from 50 to 75 cents per unit, during 1916 it has increased to $5 or $6 per unit, a unit containing 1 per cent. of K_2O for every ton of material.

In the following table is given the cost of the higher grades of German potash before the war, a discount of 15.5 per cent. being granted to purchasers of large quantities in bulk, or 15 per cent. if delivered in bags.

	Per short ton	
	1912–13	1914
Muriate of potash (80 per cent. KCl, 50 per cent. K_2O)	$38.05	$39.07
Sulphate of potash (90 per cent. K_2SO_4, 48 per cent. K_2O)	$46.30	$47.59
Manure salts (20 per cent. K_2O)	$13.30	$13.58
Kainite (12.4 per cent. K_2O)	$ 8.25	$ 8.36

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[1] H. S. Gale, U. S. Geol. Surv. Bull. 666 N, p. 2.

[2] Ibid. Mineral Resources, U.S., 1917, Part II, p. 408.

[3] Condra, G. E., Preliminary report on the potash industry of Nebraska, Nebraska Conservation and Soil Survey, Bull. 8, Lincoln, 1918.

CHAPTER XII

PLAYA DEPOSITS OF COMPLEX SALTS

We must now turn to a group of salt deposits found chiefly in playas, the origin of which is more complex than that of any so far discussed. They include especially the boron and nitrate salts, exclusive of those known to be primarily of volcanic origin. These latter will be discussed in Chapter XV.

THE SALT PLAYAS OF NEVADA AND CALIFORNIA

In western Nevada (especially Esmeralda County), and in southeastern California (Inyo and San Bernardino Counties, etc.), are a number of playas generally dry during the summer but covered by a few inches of water during the wet season, constituting what is locally known as salt "marshes." (Fig. 92.) Similar playas also occur in the semi-arid region of southern Oregon, and they are found in many portions of the old world.

The west American region is within the belt of westerly winds, which are intercepted by the Sierra Nevada ranges and the San Bernardino and other mountains, making this region for the most part one of extensive deserts. One of these, Death Valley, in Inyo County, California, is the dry bed of a salt lake and lies 160 feet below sea level, while others are thousands of feet above the sea. In San Bernardino and adjoining counties to the west lies the Mohave Desert which abounds in these dry playas. Although only partly explored, a number of these playas are known to carry extensive deposits of desert salts and some of them have been worked for commercial purposes. The best known of these playas are, Columbus Marsh, Rhodes Marsh, Teel's Marsh, Fish Lake and Silver Peak Marsh in Esmeralda County, Nevada; and Death and Saline Valleys in Inyo County; and Searles Marsh in San Bernardino County, California. The salts, according to

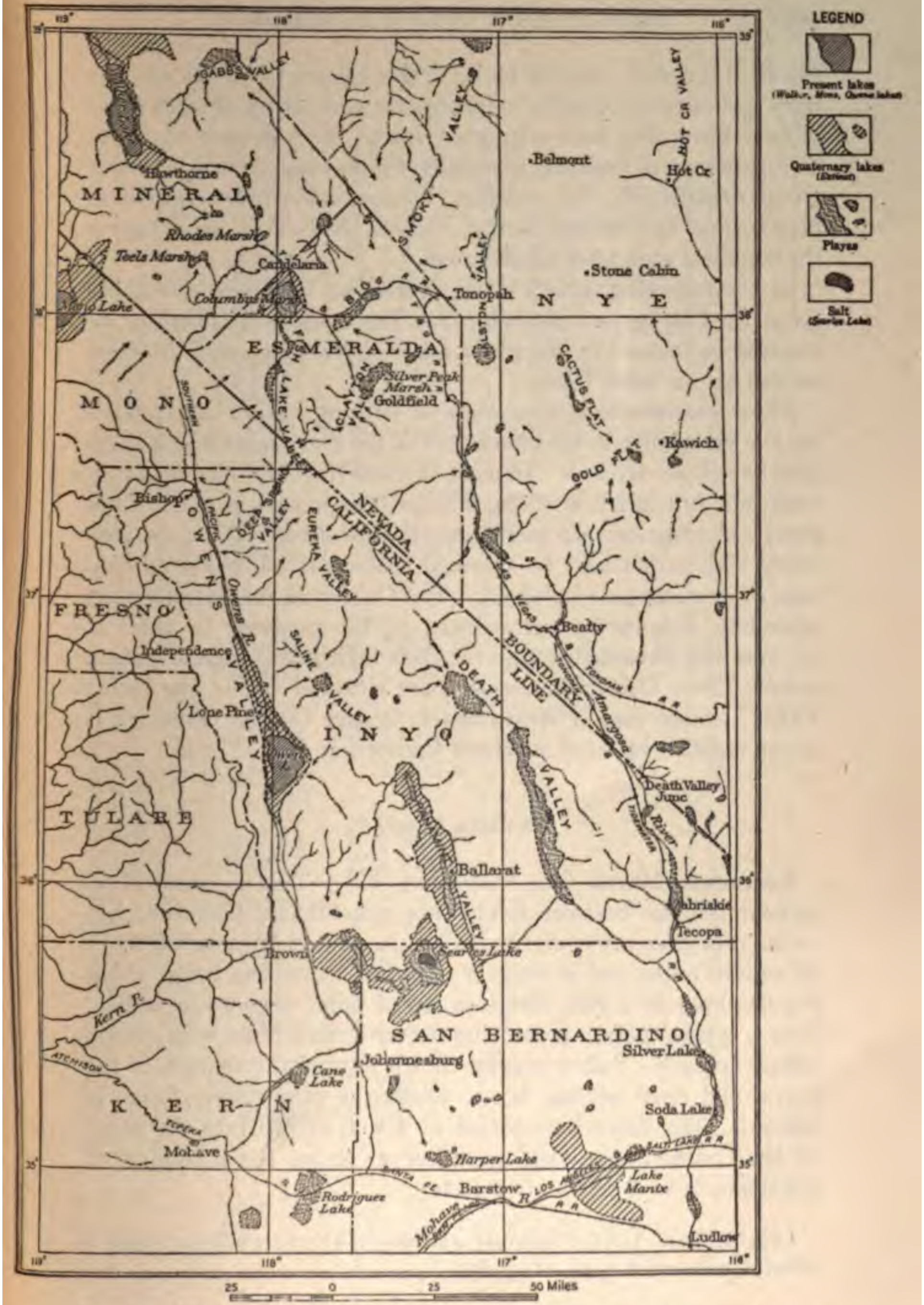

FIG. 92.—Map showing the location of the principal saline lakes and playas (marshes) in S. California and S. W. Nevada. (*After Gale.*)

M. R. Campbell, appear to be derived from leachings of Tertiary sediments, probably in large part pyroclastics, though other sources have also been suggested for at least a part of them. The presence of borates, especially the sodium borate or borax ($Na_2B_4O_7.10H_2O$), the calcium borate, colemanite ($Ca_2B_6O_{11}.5H_2O$), and the double borate, ulexite ($NaCaB_5O_9.8H_2O$) gives these playas an added significance.

In the following table a series of analyses (selected from those given by Clarke) are reproduced. They represent alkaline incrustations formed by the playa lakes of Nevada and California, as well as one from Utah.

These incrustations thus show a striking variability, reflecting the variability in the characters of the rocks from which these salts have been derived. In most of them Na_2CO_3 is the predominant salt, but in a few of them Na_2SO_4 is present in equal if not greater abundance. In such cases the content of NaCl is also generally high and it may be assumed that contributions from connate sources are here involved. The California incrustations are especially noteworthy on account of the presence in them of nitrates and phosphates, and for their high percentage of potash salts. These California deposits are situated within the Great Valley, except that of Westminster, Orange County (*I*) which is in the coastal region of southern California.

NEVADA PLAYAS

Columbus Marsh (see Map, Fig. 92).—This is situated on or near the line between Esmeralda and Mineral Counties, Nevada, near the town of Coaldale. It covers an area of 35 or 40 square miles and is roughly elliptical in outline being about 9 miles long in a NS. direction, by 6 miles or more in width.[1] It is a typical playa, presenting a broad mud plain with rough, lumpy surface. Salt is chiefly shown around the margin of the playa and here several borax producing plants were formerly located. The following section of a well drilled into the playa by the United States Geological Survey shows the characters of the deposits to a depth of 82 feet.

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[1] Phalen (Bull. U.S.G.S. 669) gives an area of 30 square miles, a length of about 8 miles and a width of 6 miles.

TABLE LXIX.—ANALYSES OF INCRUSTATIONS ON PLAYAS OF NEVADA, CALIFORNIA, AND UTAH

	Nevada playas							California playas				Utah
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*
	West arm, Black Rock Desert, Nev.	Ruby Valley, Nev.	Antelope Springs, Nev.	Near Peko, Nev., Humboldt River	Brown's Station, Nev., Humboldt Lake	North arm old Walker Lake, Nev.	Five miles west Black Rock, Nev.	Visalia, Tulare County, Cal.	Westminster, Orange County, Cal.	Experiment Station, Tulare County, Cal.	Merced Bottoms, Merced County, Cal.	Valley of Deep Creek, Utah
Na_2CO_3	52.10	58.69	25.95	48.99	7.02	72.69	9.06	65.72	66.22	32.58	75.95	25.12
$NaHCO_3$	.....	8.09	14.35	36.01	11.13	......	......	.....	.....	.....	.....	14.76
Na_2SO_4	27.55	28.32	33.31	4.42	49.67	17.49	27.05	.....	.....	25.28	4.67	17.43
$NaCl$	18.47	2.11	24.51	7.24	20.88	2.53	59.32	3.98	10.57	14.75	1.46	38.01
$Na_2B_4O_7$	.....	.....	.....	3.34	11.30	4.15	1.00					
$NaNO_3$	.....	.....	.....	.....	.....	....	....	.....	.....	19.78	12.98	
NaH_2PO_4	.....	.....	.....	.....	.....	....	....	8.42	.....	2.25	4.94	
K_2SO_4	.....	2.79	1.88	.....	.....	....	....	20.23	20.63	3.95	.....	4.68
K_2CO_3	.....	.....	.....	.....	.....	....	....	.....	6.59			
KCl	.....	.....	.....	.....	.....	1.18	1.39					
$MgSO_4$	.....	.....	.....	.....	.....	....	....	1.65				
$(NH_4)_2CO_3$	.....	.....	.....	.....	.....	....	....	.....	.....	1.41		
SiO_2	.....	.....	.....	.....	.....	1.96	2.18					
Total	98.12	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Soluble portion	.....	.....	.....	.....	.....	29.78%	23.102%					

SECTION OF U.S.G.S. WELL, 800, COLUMBUS MARSH, NEVADA

	Thickness, feet	Depth, feet
1. Surface, salt crust like that formerly worked for borax	0.5	0.5
2. Sand, light brown	1.5	2.0
3. Sand and clay, light yellow, dry	4.0	6.0
4. Clay, dark blue, smooth	1.0	7.0
5. Mud, black, smooth, sticky	5.0	12.0
6. Mud, black, smooth, wet	4.0	16.0
7. Sand, black, wet	3.0	19.0
8. Gravel, fine, containing crystals	1.5	20.5
9. Sand, fine, containing crystals	3.0	23.5
10. Clay and sand, light blue, containing hard, coarse particles	7.5	31.0
11. Clay, light gray, containing hard, coarse particles	4.0	35.0
12. Clay, black and yellow, containing hard, coarse particles	3.0	38.0
13. Clay, dark blue, containing hard, coarse particles, soft and wet	6.0	44.0
14. Clay, black, containing hard, coarse particles, soft and wet	3.0	47.0
15. Clay, light gray and black, smooth, soft and wet	1.0	48.0
16. Clay and mud, black, containing coarse, hard particles, wet	5.0	53.0
17. Clay, smooth, black, dry	4.0	57.0
18. Clay, smooth, black and yellow, dry	4.0	61.0
19. Clay, smooth, light yellow, dry	4.0	65.0
20. Clay, smooth, dark bottle green, dry	4.0	69.0
21. Clay, smooth, yellowish green, and black, dry	5.0	74.0
22. Sand, quicksand, fine running sand	8.0	82.0

Water was found at 6 feet with a salinity of 52.3 permille, at 16 feet 7.10 ‰, at 19 feet 6.10 ‰, at 48 feet 8.20 ‰, and at 74 feet 4.00 ‰. In another well, water with a salinity as high as 247.9 ‰ was obtained at 12 feet below the surface. These brines carry from 1.53 to 5.96 per cent. of K_2O. The muds, on the other hand, carried a much higher percentage, as might be expected from the absorptive power of mud for potash. Expressed in percentages of soluble material in the mud, this in some cases ranged over 20 per cent. K_2O, one analysis giving 25.18 per cent. More generally, however, the K_2O content of the mud analyzed ranged between 3 and 5 per cent. The soluble material of the mud ranged from about 5 to nearly 27 per cent. of the total, with averages as shown in

Table LXX, where the averages of the percentage of K_2O in the soluble material of the sample is also given.

TABLE LXX.—K_2O CONTENT OF THE SOLUBLE MATERIAL OF THE MUD FROM COLUMBUS MARSH

	Average soluble material	Average per cent. K_2O in soluble material
Average 15 anal. well 200	9.74	6.64% K_2O
Average 13 anal. well 300	18.27	4.34% K_2O
Average 8 anal. well 400	8.41	11.75% K_2O
Average 11 anal. well 500	12.87	5.63% K_2O
Average 11 anal. well 600	14.37	5.01% K_2O
Total average of 58 analyses	12.76	6.244% K_2O

Rhodes Marsh (Fig. 92, 93).—This lies north of Columbus Marsh in the same general desert region. The central part of this playa, which is nearly circular with diameters of 2½ to 3 miles, is occupied by a bed of sodium chloride (about 1 square mile in extent), around which there are deposits of sodium sulphate, while outside of this occurs a zone in which borax and ulexite are found.[1] Common salt is found nearly everywhere, more

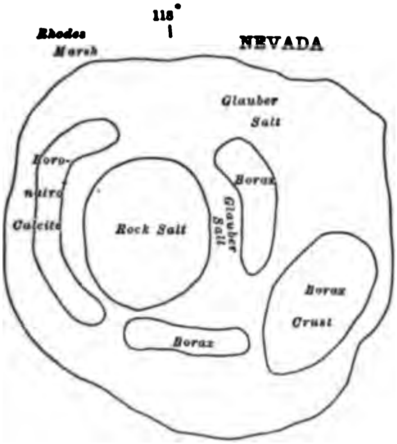

FIG. 93.—Sketch map of Rhodes Marsh, Nevada.

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[1] Joseph Le Conte in H. G. Hanks, Report on the Borax Deposits of California and Nevada, 3d Ann. Report State Mineralogist of California, 1883, pp. 1-111 (51).

Campbell, M., Borax Deposits in Eastern California, Bull. U.S.G.S. 213, pp. 401, 405, 1903.

or less mingled with the other salts. Borax occurs in three forms: (1) as a *borax crust* from one to three inches thick, more or less mingled with earth; (2) as *tincal*, in crystals in the mud below the salt; (3) as *ulexite* or borate of soda and lime. This occurs in a semicircular area around the salt, in the "cotton ball" form embedded in a wet, stiff clay.

The sulphate of soda occurs as a solid, white, ice-like layer a short distance below the surface and close to the central salt [illegible] completely surrounding it except on the west. It has a considerable thickness. Carbonate of soda has also been found in one place. The borax is apparently derived from springs, some of which still occur in the playa.

The following analyses of crude borax from this marsh are from samples taken (*a*) from the southeastern part of the playa, covering an area of about 40 acres and from 1 to 5 inches thick, and (*b*) north of the preceding, from an area of 100 acres and [illegible] to 6 inches thick.

Sample *c* is from the vicinity of the salt bed, and *d* represents the salt crust from 2 to 6 inches thick which overlies a fine and large deposit of borate of lime.

TABLE LXXI.—ANALYSES OF BORAX FROM RHODES MARSH, NEVADA

	a	*b*	*c*	*d*
Borate of sodium	40.06	57.20	14.6	15.03
Borate of calcium	1.16	5.80		
Sulphate of sodium	16.00	10.70	30.5	20.10
Carbonate of sodium	5.00	......	Trace	8.07
Chloride of sodium	8.07	9.00	26.6	15.90
Organic matter, sand and iron	29.71	17.30	38.3	40.88
	100.00	100.00	100.00	100.00

Teel's Marsh.—This lies about 16 miles northwest from Columbus Marsh and has been one of the most productive borax fields of the western states. Like others, it is a dry playa with a soft, clayey surface, formed by a deposit of crude borax. It covers an area 2½ miles wide by 5 or 6 in length. Its thickness varies from half an inch to 18 inches (map, Fig. 92).

Fish Lake.—This is a small basin situated about 25 miles south of Columbus. It is, like the others, a playa in which crude borax is the main deposit, but the brines are high in potash, containing from 13.40 to 14.48 per cent. of KCl (map, Fig. 92).

Silver Peak Marsh.—This marsh lies 30 miles southeast of Columbus and has an area of about 32 square miles. Its deposits, unlike those of the other marshes of this region, are largely sodium chloride (94.71 per cent.) with 1.16 per cent. $CaSO_4$ and 1.26 per cent. KCl. Borax ($Na_2B_4O_7$) so characteristic of the other marshes, is present only in minute quantities (0.07 per cent.). It has been held by Spurr that the NaCl here is largely derived from hot saline springs. (For fuller description see Vol. II, where other salt deposits of this region are also discussed.) (See map, Fig. 92.)

CALIFORNIA PLAYAS

Death Valley (see Fig. 92).—This remarkable valley is a narrow, deep trough apparently a fault trough or graben a hundred miles or more in length, which lies between high mountain ranges in the eastern part of Inyo County, California, its northern end extending to or across the Nevada line. The deepest part of the valley, where the salt flats are located, lies from 274 to 280 feet below sea level. In this section, which occupies the southern half of the valley, the part below sea level has a very uniform width of from 6 to 7 miles, while the part which lies more than 200 feet below the sea has a width varying from 5 to 6 miles. The bounding mountains on either side rise to 5,000 or 6,000 feet or more above the sea, and the 4,000-foot contours on opposite sides of the valley are in places less than 15 miles apart (see map, Fig. 94). On the east the valley is bounded by the Funeral Mountains which consist in part of Palæozoic limestones, shales, and quartzites. These are strongly disturbed, striking at right angles to the direction of the mountain face in the northern part of the valley, and dipping generally to the southeast from 30° to 60°. The face of the mountain fronting the northern part of Death Valley and perhaps of Mesquite Valley, is a great fault scarp. Extending diagonally across Funeral Mountain from southeast to northwest is a belt of Tertiary sediments consisting of clays, sands, and gravels with many volcanic tuffs and intrusive lava sheets, toward the base of the series. The clastics were apparently derived from the Palæozoic strata upon which they lie. Interbedded with them is a stratum of Colemanite

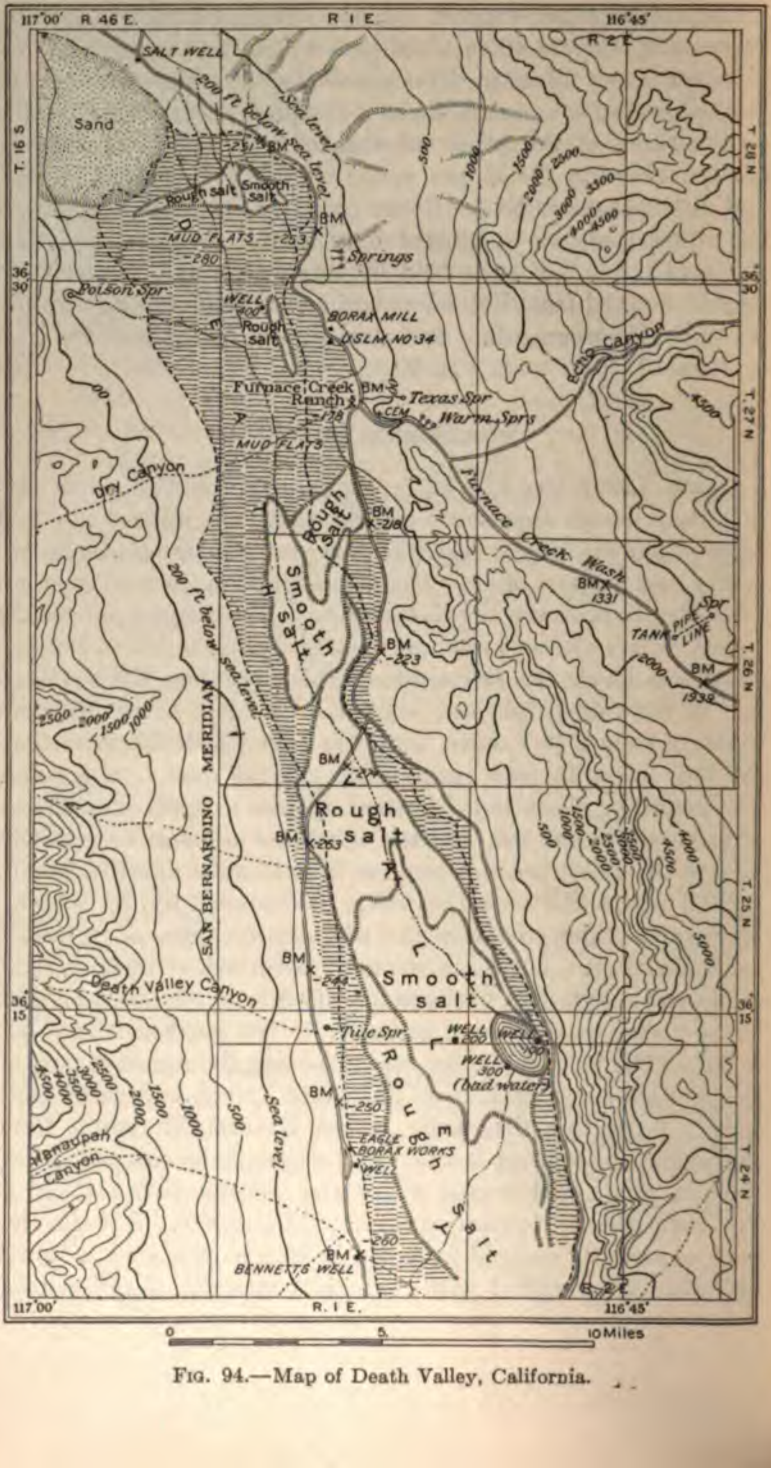

FIG. 94.—Map of Death Valley, California.

(borate of lime), which, though probably not continuous, shows in outcrop in a number of places across the mountains, a distance of at least 25 miles. This constitutes the largest deposit in the country, and probably the largest in the world (Campbell, 1902).

"At no point is it a solid regular bed, but it consists of irregular masses and stringers of Colemanite, embedded in clay. The crystals are small, seldom exceeding a quarter of an inch in diameter, and the large masses are nearly pure."[1]

In thickness, the bed varies from a few inches to 20 feet. A bed of Boracite 60 feet thick is reported 9 miles up Furnace Creek.

The Tertiary beds dip at angles of 20° to 45° toward the northeast. On the north they are limited by an abrupt mountain wall of Palæozoic strata, rising 3,000 to 4,000 feet above the Tertiaries. This face is apparently the continuation of the fault scarp of the northern Death Valley.

Armagosa River enters Death Valley from the south, while Mohave River, its normal tributary, ends today in a small ephemeral water body known as Soda Lake. From the east, Furnace Creek, a wash generally dry, enters the deeper part of the basin over the Tertiary strata. These streams carry saline material taken into solution from the desert region, into the basin, where the waters evaporate, leaving the salts. According to the recent investigations by the United States Geological Survey[2] there is no evidence that Death Valley was ever the site of a large lake; evaporation seems to have been sufficient in the past, as it is today, to prevent the accumulation of standing water. While much of the salt is probably of connate origin, some of it is believed to be derived from the solution of salt beds in the Tertiary, but Gale does not think that this is necessarily an important source.[3]

The floor of the deeper part of the valley is covered with an immense deposit of saline material which extends for many miles from north to south. "At the very lowest part of the valley, or so-called sink, there is an irregular area several miles across which is usually a smooth field of snowy white salt." This is occasionally flooded by storm waters, which redissolve the salt,

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[1] Campbell, M. R., Bull. U.S.G.S. 213, p. 404.

[2] Hoyt S. Gale, Prospecting for Potash in Death Valley, California, Bull. U.S.G.S. 504-N, pp. 11-19.

[3] *Loc. cit.*, Hoyt, S. Gale, p. 13.

CHAPTER XII

PLAYA DEPOSITS OF COMPLEX SALTS

We must now turn to a group of salt deposits found chiefly in playas, the origin of which is more complex than that of any so far discussed. They include especially the boron and nitrate salts, exclusive of those known to be primarily of volcanic origin. These latter will be discussed in Chapter XV.

THE SALT PLAYAS OF NEVADA AND CALIFORNIA

In western Nevada (especially Esmeralda County), and in southeastern California (Inyo and San Bernardino Counties, etc.), are a number of playas generally dry during the summer but covered by a few inches of water during the wet season, constituting what is locally known as salt "marshes." (Fig. 92.) Similar playas also occur in the semi-arid region of southern Oregon, and they are found in many portions of the old world.

The west American region is within the belt of westerly winds, which are intercepted by the Sierra Nevada ranges and the San Bernardino and other mountains, making this region for the most part one of extensive deserts. One of these, Death Valley, in Inyo County, California, is the dry bed of a salt lake and lies 160 feet below sea level, while others are thousands of feet above the sea. In San Bernardino and adjoining counties to the west lies the Mohave Desert which abounds in these dry playas. Although only partly explored, a number of these playas are known to carry extensive deposits of desert salts and some of them have been worked for commercial purposes. The best known of these playas are, Columbus Marsh, Rhodes Marsh, Teel's Marsh, Fish Lake and Silver Peak Marsh in Esmeralda County, Nevada; and Death and Saline Valleys in Inyo County; and Searles Marsh in San Bernardino County, California. The salts, according to

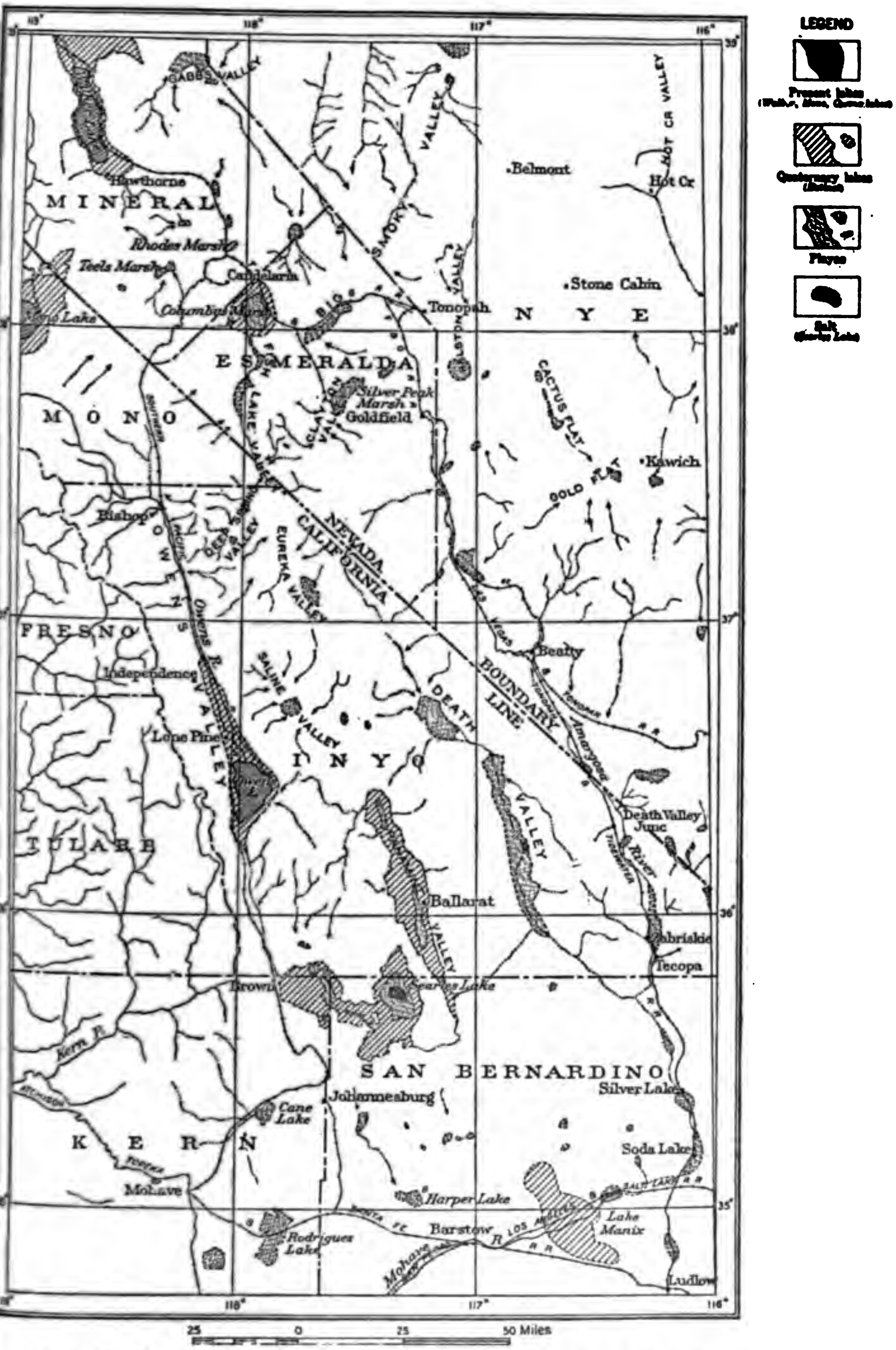

FIG. 92.—Map showing the location of the principal saline lakes and playas (marshes) in S. California and S. W. Nevada. (*After Gale.*)

M. R. Campbell, appear to be derived from leachings of Tertiary sediments, probably in large part pyroclastics, though other sources have also been suggested for at least a part of them. The presence of borates, especially the sodium borate or borax ($Na_2B_4O_7.10H_2O$), the calcium borate, colemanite ($Ca_2B_6O_{11}.5H_2O$), and the double borate, ulexite ($NaCaB_5O_9.8H_2O$) gives these playas an added significance.

In the following table a series of analyses (selected from those given by Clarke) are reproduced. They represent alkaline incrustations formed by the playa lakes of Nevada and California, as well as one from Utah.

These incrustations thus show a striking variability, reflecting the variability in the characters of the rocks from which these salts have been derived. In most of them Na_2CO_3 is the predominant salt, but in a few of them Na_2SO_4 is present in equal if not greater abundance. In such cases the content of NaCl is also generally high and it may be assumed that contributions from connate sources are here involved. The California incrustations are especially noteworthy on account of the presence in them of nitrates and phosphates, and for their high percentage of potash salts. These California deposits are situated within the Great Valley, except that of Westminster, Orange County (*I*) which is in the coastal region of southern California.

NEVADA PLAYAS

Columbus Marsh (see Map, Fig. 92).—This is situated on or near the line between Esmeralda and Mineral Counties, Nevada, near the town of Coaldale. It covers an area of 35 or 40 square miles and is roughly elliptical in outline being about 9 miles long in a NS. direction, by 6 miles or more in width.[1] It is a typical playa, presenting a broad mud plain with rough, lumpy surface. Salt is chiefly shown around the margin of the playa and here several borax producing plants were formerly located. The following section of a well drilled into the playa by the United States Geological Survey shows the characters of the deposits to a depth of 82 feet.

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[1] Phalen (Bull. U.S.G.S. 669) gives an area of 30 square miles, a length of about 8 miles and a width of 6 miles.

TABLE LXIX.—ANALYSES OF INCRUSTATIONS ON PLAYAS OF NEVADA, CALIFORNIA, AND UTAH

	Nevada playas							California playas					Utah
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*
	West arm, Black Rock Desert, Nev.	**Ruby Valley, Nev.**	**Antelope Springs, Nev.**	**Near Peko, Nev., Humboldt River**	**Brown's Station, Nev., Humboldt Lake**	**North arm old Walker Lake, Nev.**	**Five miles west Black Rock, Nev.**	**Visalia, Tulare County, Cal.**	**Westminster, Orange County, Cal.**	**Experiment Station, Tulare County, Cal.**	**Merced Bottoms, Merced County, Cal.**	**Valley of Deep Creek, Utah**
Na_2CO_3......	52.10	58.69	25.95	48.99	7.02	72.69	9.06	65.72	66.22	32.58	75.95	25.12
$NaHCO_3$......	.....	8.09	14.35	36.01	11.13	......	......	.....	.....	.....	.....	14.76
Na_2SO_4......	27.55	28.32	33.31	4.42	49.67	17.49	27.05	.....	.....	25.28	4.67	17.43
NaCl.........	18.47	2.11	24.51	7.24	20.88	2.53	59.32	3.98	10.57	14.75	1.46	38.01
$Na_2B_4O_7$.....	.....	.....	.....	3.34	11.30	4.15	1.00					
$NaNO_3$......	.....	.....	.....	.....	.....	....	....	.....	.....	19.78	12.98	
NaH_2PO_4....	.....	.....	.....	.....	.....	....	....	8.42	.....	2.25	4.94	
K_2SO_4........	......	2.79	1.88	.....	.....	....	....	20.23	20.63	3.95	.....	4.68
K_2CO_3.......	.....	.....	.....	.....	.....	....	....	.....	6.59			
KCl.........	.....	.....	.....	.....	.....	1.18	1.39					
$MgSO_4$.......	.....	.....	.....	.....	.....	....	....	1.65				
$(NH_4)_2CO_3$...	.....	.....	.....	.....	.....	....	....	.....	.....	1.41		
SiO_2.........	.....	.....	.....	.....	.....	1.96	2.18					
Total......	98.12	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Soluble portion.......	.....	.....	.....	.....	.....	29.78%	23.102%					

SECTION OF U.S.G.S. WELL, 800, COLUMBUS MARSH, NEVADA

	Thickness, feet	Depth, feet
1. Surface, salt crust like that formerly worked for borax	0.5	0.5
2. Sand, light brown	1.5	2.0
3. Sand and clay, light yellow, dry	4.0	6.0
4. Clay, dark blue, smooth	1.0	7.0
5. Mud, black, smooth, sticky	5.0	12.0
6. Mud, black, smooth, wet	4.0	16.0
7. Sand, black, wet	3.0	19.0
8. Gravel, fine, containing crystals	1.5	20.5
9. Sand, fine, containing crystals	3.0	23.5
10. Clay and sand, light blue, containing hard, coarse particles	7.5	31.0
11. Clay, light gray, containing hard, coarse particles	4.0	35.0
12. Clay, black and yellow, containing hard, coarse particles	3.0	38.0
13. Clay, dark blue, containing hard, coarse particles, soft and wet	6.0	44.0
14. Clay, black, containing hard, coarse particles, soft and wet	3.0	47.0
15. Clay, light gray and black, smooth, soft and wet	1.0	48.0
16. Clay and mud, black, containing coarse, hard particles, wet	5.0	53.0
17. Clay, smooth, black, dry	4.0	57.0
18. Clay, smooth, black and yellow, dry	4.0	61.0
19. Clay, smooth, light yellow, dry	4.0	65.0
20. Clay, smooth, dark bottle green, dry	4.0	69.0
21. Clay, smooth, yellowish green, and black, dry	5.0	74.0
22. Sand, quicksand, fine running sand	8.0	82.0

Water was found at 6 feet with a salinity of 52.3 permille, at 16 feet 7.10 ‰, at 19 feet 6.10 ‰, at 48 feet 8.20 ‰, and at 74 feet 4.00 ‰. In another well, water with a salinity as high as 247.9 ‰ was obtained at 12 feet below the surface. These brines carry from 1.53 to 5.96 per cent. of K_2O. The muds, on the other hand, carried a much higher percentage, as might be expected from the absorptive power of mud for potash. Expressed in percentages of soluble material in the mud, this in some cases ranged over 20 per cent. K_2O, one analysis giving 25.18 per cent. More generally, however, the K_2O content of the mud analyzed ranged between 3 and 5 per cent. The soluble material of the mud ranged from about 5 to nearly 27 per cent. of the total, with averages as shown in

Table LXX, where the averages of the percentage of K_2O in the soluble material of the sample is also given.

TABLE LXX.—K_2O CONTENT OF THE SOLUBLE MATERIAL OF THE MUD FROM COLUMBUS MARSH

	Average soluble material	Average per cent. K_2O in soluble material
Average 15 anal. well 200	9.74	6.64% K_2O
Average 13 anal. well 300	18.27	4.34% K_2O
Average 8 anal. well 400	8.41	11.75% K_2O
Average 11 anal. well 500	12.87	5.63% K_2O
Average 11 anal. well 600	14.37	5.01% K_2O
Total average of 58 analyses	12.76	6.244% K_2O

Rhodes Marsh (Fig. 92, 93).—This lies north of Columbus Marsh in the same general desert region. The central part of this playa, which is nearly circular with diameters of 2½ to 3 miles, is occupied by a bed of sodium chloride (about 1 square mile in extent), around which there are deposits of sodium sulphate, while outside of this occurs a zone in which borax and ulexite are found.[1] Common salt is found nearly everywhere, more

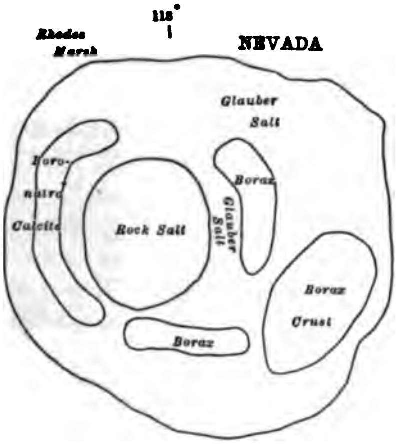

FIG. 93.—Sketch map of Rhodes Marsh, Nevada.

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[1] Joseph Le Conte in H. G. Hanks, Report on the Borax Deposits of California and Nevada, 3d Ann. Report State Mineralogist of California, 1883, pp. 1-111 (51).

Campbell, M., Borax Deposits in Eastern California, Bull. U.S.G.S. 213, pp. 401, 405, 1903.

or less mingled with the other salts. Borax occurs in three forms: (1) as a *borax crust* from one to three inches thick, more or less mingled with earth; (2) as *tincal*, in crystals in the mud below the salt; (3) as *ulexite* or borate of soda and lime. This occurs in a semicircular area around the salt, in the "cotton ball" form embedded in a wet, stiff clay.

The sulphate of soda occurs as a solid, white, ice-like layer a short distance below the surface and close to the central salt completely surrounding it except on the west. It has a considerable thickness. Carbonate of soda has also been found in one place. The borax is apparently derived from springs, some of which still occur in the playa.

The following analyses of crude borax from this marsh are from samples taken (*a*) from the southeastern part of the playa, covering an area of about 40 acres and from 1 to 5 inches thick, and (*b*) north of the preceding, from an area of 100 acres and 2 to 6 inches thick.

Sample *c* is from the vicinity of the salt bed, and *d* represents the salt crust from 2 to 6 inches thick which overlies a fine and large deposit of borate of lime.

TABLE LXXI.—ANALYSES OF BORAX FROM RHODES MARSH, NEVADA

	a	*b*	*c*	*d*
Borate of sodium......	40.06	57.20	14.6	15.03
Borate of calcium......	1.16	5.80		
Sulphate of sodium....	16.00	10.70	30.5	20.10
Carbonate of sodium..	5.00	......	Trace	8.07
Chloride of sodium....	8.07	9.00	26.6	15.90
Organic matter, sand and iron...........	29.71	17.30	38.3	40.88
	100.00	100.00	100.00	100.00

Teel's Marsh.—This lies about 16 miles northwest from Columbus Marsh and has been one of the most productive borax fields of the western states. Like others, it is a dry playa with a soft, clayey surface, formed by a deposit of crude borax. It covers an area 2½ miles wide by 5 or 6 in length. Its thickness varies from half an inch to 18 inches (map, Fig. 92).

Fish Lake.—This is a small basin situated about 25 miles south of Columbus. It is, like the others, a playa in which crude borax is the main deposit, but the brines are high in potash, containing from 13.40 to 14.48 per cent. of KCl (map, Fig. 92).

Silver Peak Marsh.—This marsh lies 30 miles southeast of Columbus and has an area of about 32 square miles. Its deposits, unlike those of the other marshes of this region, are largely sodium chloride (94.71 per cent.) with 1.16 per cent. $CaSO_4$ and 1.26 per cent. KCl. Borax ($Na_2B_4O_7$) so characteristic of the other marshes, is present only in minute quantities (0.07 per cent.). It has been held by Spurr that the NaCl here is largely derived from hot saline springs. (For fuller description see Vol. II, where other salt deposits of this region are also discussed.) (See map, Fig. 92.)

CALIFORNIA PLAYAS

Death Valley (see Fig. 92).—This remarkable valley is a narrow, deep trough apparently a fault trough or graben a hundred miles or more in length, which lies between high mountain ranges in the eastern part of Inyo County, California, its northern end extending to or across the Nevada line. The deepest part of the valley, where the salt flats are located, lies from 274 to 280 feet below sea level. In this section, which occupies the southern half of the valley, the part below sea level has a very uniform width of from 6 to 7 miles, while the part which lies more than 200 feet below the sea has a width varying from 5 to 6 miles. The bounding mountains on either side rise to 5,000 or 6,000 feet or more above the sea, and the 4,000-foot contours on opposite sides of the valley are in places less than 15 miles apart (see map, Fig. 94). On the east the valley is bounded by the Funeral Mountains which consist in part of Palæozoic limestones, shales, and quartzites. These are strongly disturbed, striking at right angles to the direction of the mountain face in the northern part of the valley, and dipping generally to the southeast from 30° to 60°. The face of the mountain fronting the northern part of Death Valley and perhaps of Mesquite Valley, is a great fault scarp. Extending diagonally across Funeral Mountain from southeast to northwest is a belt of Tertiary sediments consisting of clays, sands, and gravels with many volcanic tuffs and intrusive lava sheets, toward the base of the series. The clastics were apparently derived from the Palæozoic strata upon which they lie. Interbedded with them is a stratum of Colemanite

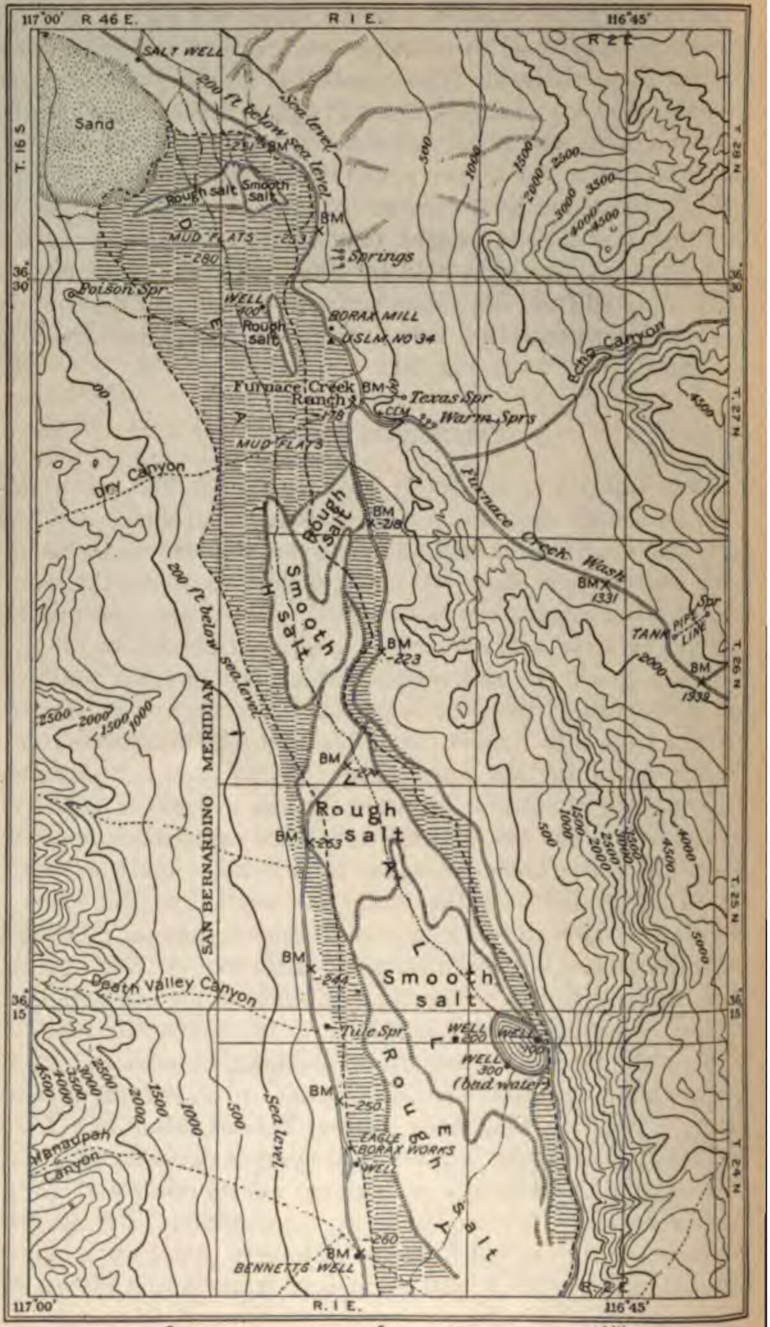

FIG. 94.—Map of Death Valley, California.

(borate of lime), which, though probably not continuous, shows in outcrop in a number of places across the mountains, a distance of at least 25 miles. This constitutes the largest deposit in the country, and probably the largest in the world (Campbell, 1902).

"At no point is it a solid regular bed, but it consists of irregular masses and stringers of Colemanite, embedded in clay. The crystals are small, seldom exceeding a quarter of an inch in diameter, and the large masses are nearly pure."[1]

In thickness, the bed varies from a few inches to 20 feet. A bed of Boracite 60 feet thick is reported 9 miles up Furnace Creek.

The Tertiary beds dip at angles of 20° to 45° toward the northeast. On the north they are limited by an abrupt mountain wall of Palæozoic strata, rising 3,000 to 4,000 feet above the Tertiaries. This face is apparently the continuation of the fault scarp of the northern Death Valley.

Armagosa River enters Death Valley from the south, while Mohave River, its normal tributary, ends today in a small ephemeral water body known as Soda Lake. From the east, Furnace Creek, a wash generally dry, enters the deeper part of the basin over the Tertiary strata. These streams carry saline material taken into solution from the desert region, into the basin, where the waters evaporate, leaving the salts. According to the recent investigations by the United States Geological Survey[2] there is no evidence that Death Valley was ever the site of a large lake; evaporation seems to have been sufficient in the past, as it is today, to prevent the accumulation of standing waters. While much of the salt is probably of connate origin, some of it is believed to be derived from the solution of salt beds in the Tertiary, but Gale does not think that this is necessarily an important source.[3]

The floor of the deeper part of the valley is covered with an immense deposit of saline material which extends for many miles from north to south. "At the very lowest part of the valley, or so-called sink, there is an irregular area several miles across which is usually a smooth field of snowy white salt." This is occasionally flooded by storm waters, which redissolve the salt, and on evaporation again leave the surface encrusted with it. Fields of rough salt occur, both north and south of this, where the salt which has been exposed for a longer time is broken into cakes and tilted at various angles, probably by the expansive force of growing crystals, and so produces an exceedingly rough surface similar to that described from other desert areas. "A river of soft mud lies between the main salt field and the valley margin, this part also being flooded occasionally by storm waters, and kept wet by the seepage of ground water from the marginal slopes." Next to the mud river is a zone of sand dunes, which passes outward into the zone of alluvial rock débris (see map, Fig. 94). The deposits in the valley bottom consist of clays and muds, covered with a crust of salt from 1½ inches to 6 inches thick. Wells sunk into these deposits by the Survey to a maximum depth of 104 feet, showed it to consist of muds commonly with salt crystals scattered through it, and with salt beds from ½ to 2½ feet thick in the upper parts. These beds are, however, not continuous, for the beds of well 200 have no representation in well 300, about a mile and a half distant, and beginning on the same bed of smooth salt. Only between 30 and 40 feet below the surface are representative beds to be found, those of well 300 being, however, much thinner. At 51 feet below the surface in well 200, a heavy series of salt beds begins, at first with some intercalated muds, but continuing for 23 feet with only a single 1-foot bed of clay with salt crystals 5 feet above the base. In well 300 these salt beds, separated by layers of clay, lie between 52 and 65 feet, the salt gradually becoming purer downward, while between 65 and 85 feet lies a solid series with, however, a 1-foot bed of clay, 2 feet above the base, and another 0.2 feet in thickness 6.8 feet above the base. In well 200 the heaviest salt is 24 feet thick, and in well 300, 20 feet, but lying at a lower level. In well 400, which lies about 18 miles north of well 200, the first salt bed, 2 feet thick, begins at 31.5 feet below the surface; while at 35 feet below the surface begins a heavy bed which has been penetrated for 12 feet. The following section (Fig. 95) gives the records of the 4 wells as constructed from the logs, their locations being shown on the map (Fig. 94). This shows well the inequality in the distribution of the salt beds, a feature eminently characteristic of desert salt deposits.

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[1] Campbell. M. R., Bull. U.S.G.S. 213. p. 404.

[2] Hoyt S. Gale, Prospecting for Potash in Death Valley, California, Bull. U.S.G.S. 504-N. pp. 11-19.

[3] *Loc. cit.*, Hoyt, S. Gale, p. 13.

An analysis of the salt from the middle of one of the rough salt surfaces, where it was nearly 3 miles wide gave the results shown in Table LXXII, on p. 274.

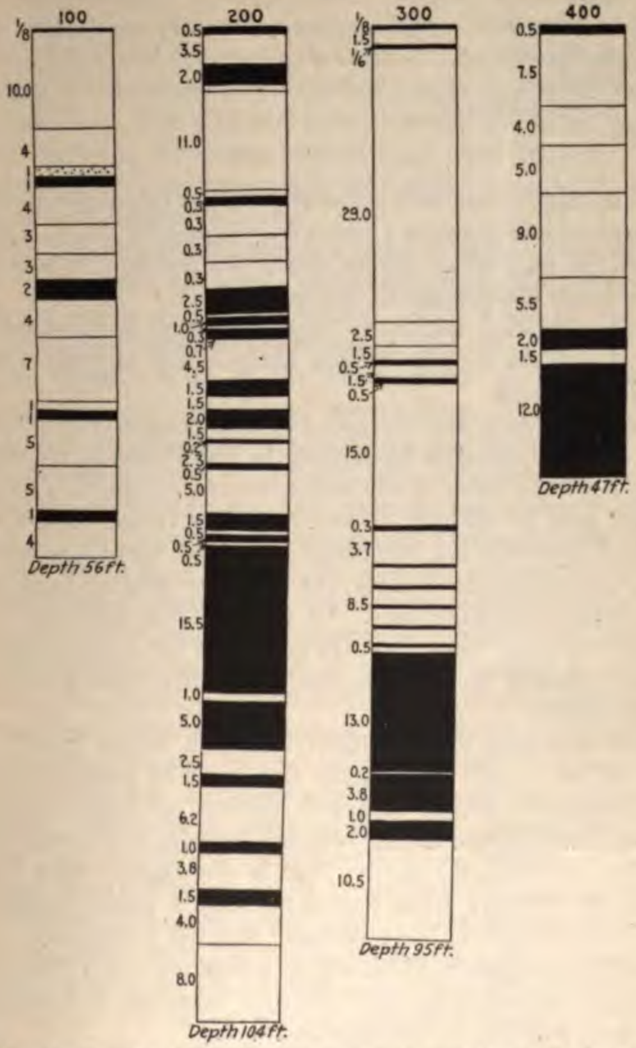

FIG. 95.—Well-sections in Death Valley. Salt in solid black; thickness in feet. (For location see map, Fig. 94.)

In none of the analyses of salts or brines from various depths was the potash very high. As a rule the K_2O content was less than 1 per cent. in the solid salt, though in a few cases rising to

TABLE LXXII.—ANALYSES OF SALT FROM DEATH VALLEY (GALE)

NaCl	94.54
KCl	0.31
Na_2SO_4	3.53
$CaSO_4.2H_2O$	0.79
Moisture	0.14
Insoluble residue	0.50
	99.81

2 or even slightly above 3 per cent. In the brines the K_2O content was generally above 1 per cent., frequently above 2, and in one case, in the surface waters, nearly 3.5 per cent. of total salts (expressed as percentages of ignited residue).

Another striking feature in these records is the complete absence of gypsum deposits, a lack noticeable in the salt deposits of all desert areas.

From a survey of the analyses and well records, Gale concludes that "the solid material underlying the lowest part of the valleys, exclusive of the floors in the water-bearing strata, to a depth of 100 feet may be assumed to average about 19 per cent. of moisture, and after this has been dried out under conditions approximately normal for the locality, the dried material averages about 65 per cent. of soluble salts. Of these soluble salts only about 0.72 per cent. has been shown to be potash (or 1.13 per cent. potassium chloride, the form in which the salt is doubtless present in this deposit)."[1]

Borax was once manufactured in Death Valley 2 or 3 miles north of the mouth of Furnace Creek. The material utilized was Colemanite, which Campbell believes has been derived by solution from the bed in the Tertiary deposits of Funeral Mountains and redeposited on the floor of the basin. The original bed in the Tertiary series was apparently a playa deposit, the source being borax-bearing springs,[2] but the Colemanite is also regarded as a replacement of limy beds of playa origin, the boracic acid being derived from fresh volcanic material, and carried to its present position by underground water.

In the Mohave Desert, about 12 miles north of Daggett, San Bernardino County, California, an extensive borax deposit occurs at a locality named Borate. The mineral is borate of lime or Colemanite and it occurs as a bedded deposit from 5 to 30 feet thick interstratified with lake and alluvial sediments. The clastic beds consist of semi-indurated clays, sandstones and coarse conglomerates, with intercalated sheets of volcanic tuff and lava. The rocks are severely folded, the folds extending in an east and west direction. The lake and alluvial strata are cut off and are infolded with the crystalline rock of the Calico District. West of Calico Valley, Colemanite has been found at a depth of 200 feet in beds of similar character.

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[1] Bull. U. S. Geol. Surv. No. 200, 1902, Engineering and Mining Journal, Vol. 74, 1902, p. 517.

[2] Campbell, Bull. U.S.G.S. 213, pp. 401-405.

The Colemanite beds appear as a series of large lumps, extending for about a mile and a half, after which they thin away. The age of the bed is probably Tertiary. This is one of the chief producing regions of borax and boracic acid in the country.

Saline Valley.—West of the northern end of Death Valley and between it and the valley of Owen's River, lies Saline Valley, a deep, narrow depression bounded on the west by the Inyo Mountain range, which separates it from Owen's Valley; on the east by Butler Mountains; and more or less enclosed on the north and south so as to form an inland drainage basin which, however, has its floor nearly 1,500 feet above sea level. From the surrounding mountains, which are partly sedimentary (Palæozoic and Triassic) rocks and partly Tertiary lavas, streams enter this valley bringing loads of débris and salts in solution (see map, Figs. 92, 96). On the eastern part of the valley floor is a playa deposit of salts and muds and occupying an area of approximately 12 square miles. Of this, about 1 square mile consists of a smooth, white salt crust, containing a small pond of salt water. This area is shown on the map. Beyond the white salt, the playa surface is formed by a rough expanse of broken and tilted blocks which form an exceedingly sharp, craggy surface. This rough salt has a dirty brown color, apparently due to wind-borne dust, while the repeated solution of the central area allowed such dust to settle out and form stratified layers below the salt crust. The upper layer of pure salt in this central area is now about 4 inches thick, being underlain by a bed of salt mud. Below that are, however, other salt layers, and there is much brine which rises to the level of the salt crust whenever a hole is dug.

Analysis of the pure salt from the central part of the playa gave the results shown in Table LXIV, on p. 277.

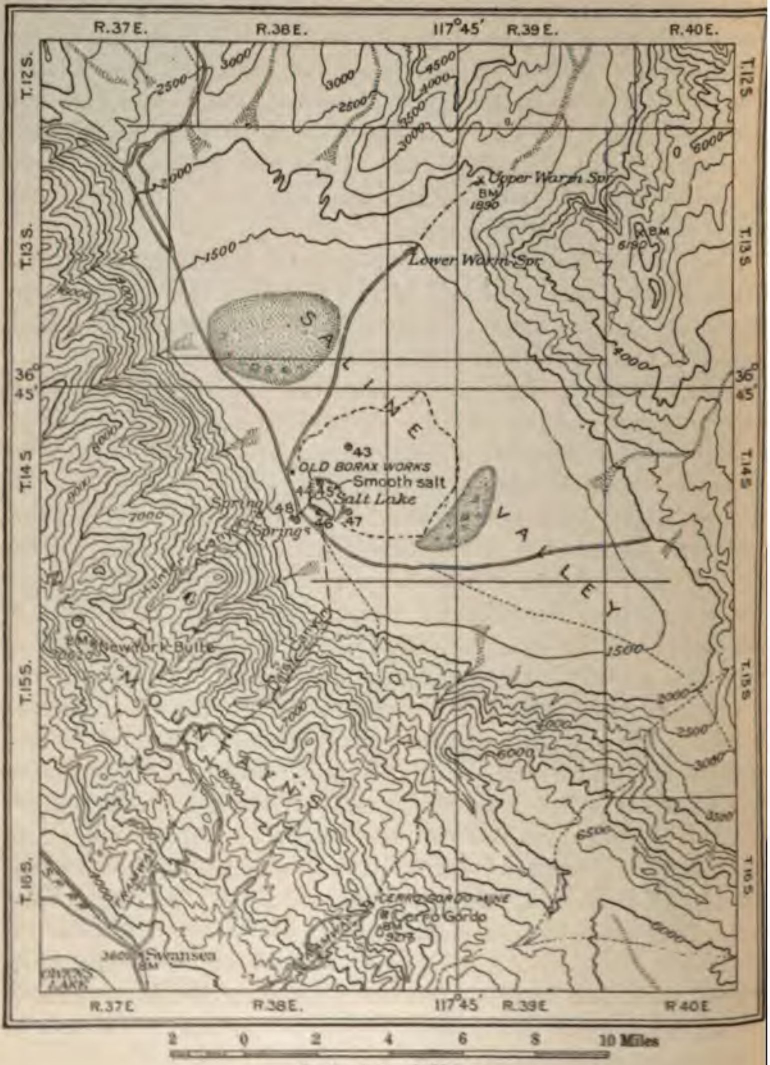

FIG. 96.—Map of Saline Valley.

TABLE LXXIII.—ANALYSIS OF SALT FROM SALINE VALLEY, CALIFORNIA

Cl	59.76		
		NaCl	98.52
Na	39.09		
		Na_2SO_4	1.02
SO_4	0.95		
		K_2SO_4	0.37
K	0.11		
H_2O	0.12		0.12
Insoluble	0.17		0.17
	100.20		100.20

There are no carbonates or bicarbonates, nor is there any calcium or magnesium in this salt. Analyses of the brines showed a low content of potash, this in the best cases amounting to 1.56 per cent. of K_2O; (2.47 per cent. KCl) and in others being almost absent (0.06 per cent. K_2O or 0.10 per cent. KCl).

Borax was formerly obtained from parts of the salt crust in the playas, but this seems to have been exhausted.

Searles Lake or Marsh (Fig. 97).—This is in many respects the most interesting of the playas so far studied and the one which has attracted the most widespread attention in recent times on account of the presence of considerable potash in the deposits. This has been estimated to comprise about 4,000,000 tons of water-soluble potash salts, and this playa is regarded as the most promising known source of potash in the United States.

The playa is situated in the northwestern part of San Bernardino County, California, in a valley formed by the northward convergence of two mountain ranges which rise to heights of 5,000 to 6,000 feet or over, above sea level; while the surface of the outer zone of the playa stands at an elevation of 1,623 feet, and that of the inner area at 1,518 feet above the sea. The surface of the playa is estimated at about 60 square miles, but the central part of firm, crusted salt which forms the main salt deposit is only 11 or 12 square miles in area, while the depth of the deposit averages about 70 feet. The basin of which this playa forms the center, was formerly occupied by a lake which had a maximum depth of 635 to 640 feet. The history of this lake, like those of so many others in the arid regions, is written in the ancient shorelines which are still preserved. Evaporation finally destroyed the lake, leaving only this playa.

The playa is dry, for the most part being flooded intermittently only by shallow water. Its surface is covered by a saline crust or crystal layer, which besides Halite and Thenardite also contains borax. Sometimes water accumulates in the depressions

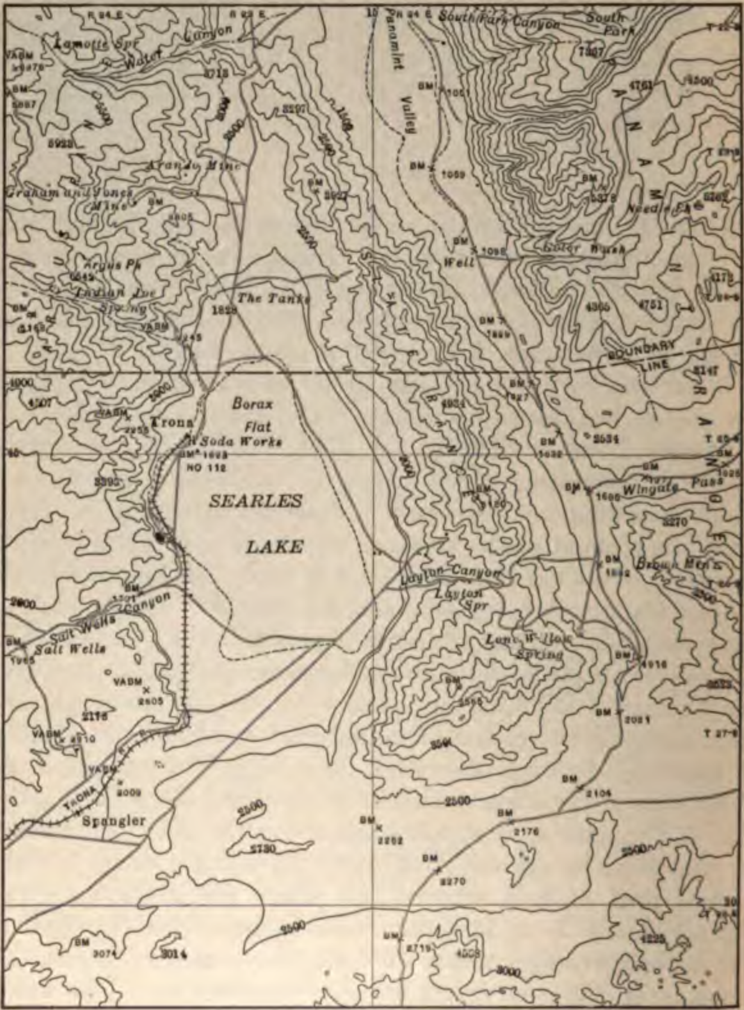

Fig. 97.—Map of Searles Lake, Cal.

of the bed, and in this the salts are dissolved. The crust is slowly renewed through capillary action which brings the soluble salts from below and allows them to crystallize on the surface.

As a result, this crust can be repeatedly worked. This has been done especially for the borax since 1873.

Borings have shown the succession of deposits in the outer zone of the playa to be as follows in descending order.[1]

1. Salt and thenardite (Na_2SO_4)	2 feet
2. Clay and volcanic sand with some hanksite ($(Na_{22}K(SO_4)_9CO_3)_2Cl$)	4 feet
3. Volcanic sand and black clay with bunches of trona ($Na_3H(CO_3)_2.2H_2O$)	8 feet
4. Volcanic sand containing glauberite ($Na_2Ca(SO_4)_2$) thenardite and a few crystals of hanksite	8 feet
5. Solid trona ($Na_3H(CO_3)_2.2H_2O$) overlain by a thin layer of very hard material	28 feet
6. Mud, smelling of hydrogen sulphide and containing layers of glauberite, soda and hanksite	20 feet
7. Clay, mixed with volcanic sand and permeated with hydrogen sulphide	230 feet +
Total	300 feet +

Subsequently in 1895 and 1896 the well was continued to a depth of nearly 628 feet through muds with occasional layers of pierssonite between 408 and 469 feet and below that more muds and clays with scattered minerals of various kinds, including calcite, halite, pierssonite, searlsite, etc. (for details see the report by H. S. Gale[2]).

In the central area, mud is much less characteristic, the deposit being in effect a solid body of salts from 60 to over 100 feet in thickness. It contains in the interstices between the salt crystals a saturated brine the volume of which is estimated to be more than 25 per cent. of that of the entire mass.[3] A well drilled through the salt crust (September 20, 1913), Well 86, gave the following succession in descending order ((Gale, p. 273).

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[1] De Groot, Tenth Ann. Report Cal. State Mining Bureau, 1890, p. 535.
G. E. Bailey, The Saline Deposits of California, Bull. 24, Cal. State Mining Bureau.

[2] Salinas in Owen's, Searles' and Panamint Basins, Southeastern California by Hoyt S. Gale, U. S. Geol. Surv. Bull. 580, 1913, pp. 251-323 (289-294).

[3] More recently it has been estimated to comprise at least 50% of the total volume of the lake, and it may even reach 75% or more. With an area of 7000 acres and a depth of 60 feet, the lake would contain about 11,000,000 short tons of potash (K_2O). As the area from which brine is derived is larger than that of the salt body, it is probable that the total amount of K_2O is more nearly 20,000,000 tons. The production at the end of 1917 was about 200 tons of high grade potash salt per month. (Gale, H. S., Mineral resources of the U. S., for 1917 Pt. II, pp. 411, 412.)

	Depth
1. Slightly muddy crystalline salts in coarse granular form, drained off the brine, apparently in large part halite in cubic crystals and broken fragments	0–5 feet
2. Clear to slightly greenish crystals, drained off the mother liquor brine, mainly showing distinct crystal forms of halite, both cubic and octahedral. Coarser grained than No. 1, size of pea to ½ inch or more in diameter	5–10 feet
3. Slushy sample consisting of salt crystals of distinct halite form ½ inch or less in size in finer granular mass of smaller crystals colored by a small admixture of dull greenish mud	10–15 feet
4. Similar in appearance to 3	15–20 feet
5. A mass of wet salt crystals, slightly mashed and colored by greenish mud, mostly showing some crystal outline, size of grains of wheat to size of corn	20–25 feet
6. Similar to sample 5, but contains double-ended hanksite crystals with other salts	25–30 feet
6*a*. Similar to 6 with less hanksite and some large, dark, distinct unidentified crystals	30–32 feet
7. Salt or saline crystals much bedaubed with dark greenish to gray wet mud	32–35 feet
8. Salt grains, crystals (halite form) and a wet mass of finer saline material, somewhat crushed and mixed with mud	35–40 feet
9. Clear, transparent salt grains, wheat size in general, including both coarser and finer material and some distinct hanksite crystals	40–45 feet
10. Salt in coarse and fine granular and cubic crystal forms, with distinct hanksite crystals, all somewhat discolored by mud	45–50 feet
11. Wet salts granular and in coarse fragments, halite and possibly also other soda (?) minerals clean from mud and drained of brine	50–55 feet
12. Same as sample 11	55–60 feet
13. White, slushy mass of salts (as if coarsely ground up) containing some larger, snowy white and a few large, very dark crystals (?)	60–65 feet
14. Same as sample 13, including a few dark crystals	65–70 feet
15. Mostly opaque white mass of salts drained of brine, not mixed or discolored with mud, suggests soda carbonate, trona (?) with few granular fragments and crystals like halite, perhaps fallen from upper part of well. This is reported to be the bottom of the salt deposit	70–75 feet

At least 200 wells have so far been sunk into this deposit and the materials taken out are undergoing study by the U. S. Geological Survey.

In the following table are given the analyses of the brines from this deposit. In the first column is given the composition of a composite sample of six brines taken from various wells and at various depths. The second column shows the average composition of six separate analyses of brines from different wells. The third column gives the composition of the brine from a single well (SE 7).[1]

TABLE LXXIV.—ANALYSES OF BRINES FROM SEARLES LAKE

	A	B	C
	Average of sample from 6 brines, W. B. Hicks	Average of 6 analyses of brines of 6 wells, Walter Van Winckle	Analysis of brine from well SE 7, W. H. Ross
K	6.17	6.34	6.07
Na	33.66	33.80	33.61
Cl	36.36	37.04	37.10
SO_4	12.86	13.00	12.99
CO_3 (combined carbonates and bicarbonates)	7.72	7.24	6.71
B_4O_7	3.23	2.50	3.01
Other constituents (Li, Mg, Al_2O_3, Fe_2O_3, SiO_2, Br, I, PO_4, As_2O_3, etc.)	?	0.08	0.51
	100.00	100.00	100.00
Total salts by summation	34.04	33.91	32.90
Specific gravity	1.2938 at 23°C.	1.2974	

A recalculation of these analyses in the form of hypothetical anhydrous salts which might be derived from such a brine, gave the following:

TABLE LXXV.—HYPOTHETICAL COMBINATION OF SALTS FROM BRINES OF SEARLES LAKE

NaCl	51.61
Na_2SO_4	19.22
Na_2CO_3	12.79
$Na_2B_4O_7$	3.23
KCl	12.07
Na_3AsO_4	0.17
	99.09

Analyses of the salts from successive levels of well SE8 have been combined as follows. Well SE8 is 1 mile due east of Well SE7 and both are near the center of the main salt deposit.

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[1] W. B. Hicks, Evaporation of Brine from Searles Lake, California, U. S. Geol. Surv. Prof. Paper 98A, 1916, pp. 1-7, Also Gale, *loc. cit.*

TABLE LXXVI.—ANALYSES OF SALTS FROM SUCCESSIVE DEPTHS IN SEARLES LAKE (WELL SE 8)

Depth in feet	0–18	18–25	25–30	30–35	35–50	50–65	65–79
$NaCl$	79.7	44.0	47.3	42.7	43.5	82.8	19.0
Na_2SO_4	7.6	30.5	28.1	17.1	22.3	10.6	7.3
Na_2CO_3	3.2	14.8	10.6	19.1	9.5	3.2	40.3
$NaHCO_3$	0.0	2.5	0.0	5.9	2.5	0.8	18.5
NaB_4O_7	Trace	1.0	2.0	2.0	5.5	Trace	0.5
H_2O	3.3	5.8	10.6	10.2	15.3	2.6	14.4
Insoluble, mud, etc.	0.2	1.4	1.4	3.0	1.4	Trace	Trace

Minerals of Searles Lake.—A considerable number of mineral species or salts have been found in the deposits of Searles Marsh. These are given in the subjoined list which should be compared with the list of minerals obtained from the evaporation of marine waters as shown by the Stassfurt deposits (Chapter XXIV). The difference is a marked one and seems to emphasize the difference in origin, for the deposits of Searles Marsh are to a very large degree decomposition products of igneous and other rocks, ocean water having played no direct part in their development, and probably a very minor indirect part, since the alterations which the old marine sediments of this part of the state have undergone have probably destroyed or removed their connate salts in large measure.

LIST OF SPECIES OF SALTS FOUND IN SEARLES LAKE, SAN BERNARDINO COUNTY, CALIFORNIA

I. Sulphates:	
* Anhydrite	$CaSO_4$
* Gypsum	$CaSO_4.2H_2O$
* Celestite	$SrSO_4$
Thenardite	Na_2SO_4
Mirabilite	$Na_2SO_4.10H_2O$
* Glauberite	$Na_2SO_4.CaSO_4$
II. Borates:	
Borax	$Na_2B_4O_7.10H_2O$
Colemanite (?)[1]	$Ca_2B_6O_{11}.5H_2O$
III. Carbonates:	
Calcite	$CaCO_3$
Natron	$Na_2CO_3.10H_2O$

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[1] The occurrence of Colemanite has been doubted.

IV. **Double Carbonates:**	
Trona	$Na_2CO_3.NaHCO_3.2H_2O$
Gaylussite	$Na_2CO_3.CaCO_3.2H_2O$
Pierssonite	$Na_2CO_3.CaCO_3.5H_2O$
Dolomite	$MgCO_3.CaCO_3$
V. **Chlorides:**	
* **Halite**	NaCl
VI. **Nitrates:**[1]	
Soda niter	$NaNO_3$
VII. **Borosilicates:**	
Searlesite	$Na_2O.B_2O_3.4SiO_2.2H_2O$
VIII. **Triple Salts:**	
Sulphohalite	$2(Na_2SO_4).NaCl.NaF$ or $Na_6(SO_4)_2.ClF$
Hanksite	$9(Na_2SO_4).2(Na_2CO_3).KCl$
Northupite	$Na_2CO_3.NaCl.MgCO_3$
Tychite	$3(NaCO_3).MgCO_3.MgSO_4$

Comments on the List.—Those marked by an asterisk (*) are also found in the Stassfurt deposits of marine salts and it will be seen that they are with one or two exceptions mineral species of wide distribution and almost universal presence in salt deposits of all types. Nothing could more strongly emphasize the difference of the present series from the deposits of marine origin.

The presence of the borates and nitrates in these deposits demands a closer consideration than has yet been given this subject. The borates may be regarded as leached decomposition products from rocks containing tourmaline,[2] and other borosilicates but such source has not been directly traced for the saline borates under consideration.

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[1] The niter has been reported from the clay hills at the south end of the basin, but does not, so far as known, occur in association with the main salt deposit.

[2] The chief borosilicates are:

Tourmaline: $R_{18}.B_2(SiO_5)_4$. R chiefly Al, K, Mn, Ca, Mg, Li with B_2O_3 ranging around 10 per cent. occurs in granites, pegmatites and more rarely porphyries and lavas, also in mica schists, gneiss, phyllites, clay slates, and in zones of contact metamorphism.

Datolite: $HCaBSiO_5$ with 21.8 per cent. B_2O_3 occurs as a secondary mineral in basalts, gabbros, etc., and in gneiss and amphibolite. Also in zones of contact metamorphism.

Axinite: $Ca_7Al_4B_2(SiO_4)_8$ with B_2O_3 in the neighborhood of 5 per cent., occurs in cavities in some granites and diabases; also in zones of metamorphism in contact with these rocks.

Danburite: $CaB_2(SiO_4)_2$, with 28.4 per cent. B_2O_3, occurs in granitic rocks.

Dumortierite: $Al_{20}Si_7O_{44}$, with part of the Al replaced by boron. B_2O_3 reaches 6.14 per cent. in dumortierite from Harlem, N. Y. Occurs chiefly in granitic pegmatite and gneiss and in quartzose rocks (Arizona, Washington).

The nitrates are not found in association with the other salts, but in the immediate vicinity. The nitrogen might be regarded as of organic origin, and the boron as possibly derived from connate sources, but neither of these hypotheses seems very satisfactory. The influence of magmatic waters or of fumaroles might account for both, and such sources are not uncommon in the region under consideration. Nevertheless they have not been actually determined in connection with the deposits of Searles Marsh. The presence of ammonium compounds, however, 15 feet below the crust or crystal layer, lends some probability to this supposition. According to our present understanding of the sources and distribution of such materials, we may classify them as follows (Clarke):

1. *Marine Origin.*—Characterized by magnesium borates and double salts with magnesium and some other base. This is the type of borates found in the Stassfurt beds (see Chapter XXIV).

2. *Lake Bed or Playa Deposits of Complex Origin* (*Probably in the Main Decomposition*).—Characterized by calcium borates with nitrates near by. To this type belong the California and Nevada playas. The presence of Colemanite in the deposits of Searles Lake has, however, been denied.

3. *Volcanic* (*Magmatic*) *Waters and Fumaroles.*—Borates primarily of calcium and sodium accompanied by ammonium compounds. This is the character of the Tuscan and Tibetan borax deposits (see Chapter XV).

The paragenesis of the minerals of a playa, whose salts are not of marine origin but mainly decomposition products, has not yet been investigated. It is a problem more complicated than that of the marine salts studied by Van't Hoff, though the principles enunciated by that investigator are no doubt applicable to the present case. The chief difficulty lies in the fact that we are not able to start with a solution of known composition as in the case of sea water which was the source of the Stassfurt salts. Perhaps the first step in the solution of this problem is the investigation of the history of the playa basin and the determination whether or not the sea had access to it at any time. This is a problem for the geologist, as is also the question whether or not magmatic waters played any part in the history of the deposits. After that the problem becomes one for the physical chemist. It is much to be hoped that the whole problem will soon receive the attention it deserves.[1]

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[1] For Other Saline Deposits of California see Vol. II.

CHAPTER XIII

THE OCCURRENCE AND ORIGIN OF NITRATE DEPOSITS

The nitrates are among the most puzzling of the playa deposits, and about the origin of no other except perhaps the borates has there existed a greater difference of opinion among students of salt deposits.

THE ATMOSPHERE AS A SOURCE OF NITROGEN

The nitrogen of nitrates is probably in most cases derived from the atmosphere, either through the agency of animals and plants which appropriate it to form nitrogenous compounds, through electrical separation from the atmosphere, or in some other way. Much nitrogen is also derived from volcanic sources, as is shown by analyses of the gases from Kilauea and other volcanoes, of which nitrogen (N_2) in some cases constitutes as much as 63.3 per cent.

The average volumetric composition of the atmosphere is shown in the following table.

TABLE LXXVII.—AVERAGE VOLUMETRIC COMPOSITION OF THE ATMOSPHERE, IN PARTS PER 10,000

Oxygen	2,065.940	Ozone	0.015
Nitrogen	7,711.600	Aqueous vapor	140.000
Argon (about)	79.000	Nitric acid	0.080
Carbon dioxide	3.360	Ammonia	0.005

Free hydrogen, up to 2 parts in 10,000 also frequently occurs, and some other minor constituents (methane, benzine, formaldehyde and sulphur compounds) are also found.

Electrical discharges in the air probably convert some of the oxygen into the allotropic modification ozone, and form besides this, hydrogen dioxide and oxides of nitrogen. These latter, with the moisture of the air, form nitric and nitrous acids, which when brought to the earth by rains attack the rocks and soil forming nitrates and nitrites. The ozone and the hydrogen dioxide are powerful oxidizing agents, and they will react on organic matter suspended in the air and transform it into carbon dioxide, water, and probably ammonium nitrate.[1]

ORGANIC SOURCES OF NITROGEN

Organisms, especially plants, fix a certain amount of nitrogen from the air by the formation of nitrogenous compounds. Analyses of plants show the presence in the composition of their tissues of nitrogen up to in some cases nearly 3 per cent. A few of these analyses are given in the following table, calculated to an ash-free basis (Clarke).

Semper and Michels held that the nitrates of Chile "are formed by the oxidation of the nitrogen of the air through the electrostatic tension that is such a marked accompaniment of the frequent coast fogs or *camanchacas*, that roll in over the nitrate pampa at night."[2] The electric storms of the Andes have also been regarded as an important cause of the formation of nitrogen compounds from the atmosphere.

TABLE LXXVIII.—COMPOSITION OF VARIOUS TYPES OF PLANTS

	A	B	C	D	E
	Average of 36 analyses, 5 different weeds	Average analyses of 5 acrogens[3]	Sphagnum	Light peat near surface	Black peat
C	51.21	48.83	49.88	50.33	59.71
H	6.24	6.37	6.54	5.99	5.27
O	41.45	42.63	42.42	42.63	32.07
N	1.10	2.17	1.16	1.05	2.95
	100.00	100.00	100.00	100.00	100.00

The Chilean nitrates were at one time assumed to be derived from seaweeds which had accumulated in that region while it stood at or below sea-level.

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[1] Hess, W. H. The Origin of Nitrates in Cavern Earth, Journ. Geol., Vol. 8, 1900, pp. 120–134.

Nichols, H. W., Nitrates in Cave Earths, Ibid., Vol. 9, 1901, pp. 236–243.

Merrill, G. P., "Rocks, Rock Weathering and Soils," 1897, pp. 372–373.

Merrill, G. P., "The Non-metallic Minerals, Their Occurrence and Uses," 2d Ed., 1910, pp. 315–321.

[2] Miller and Singewald, Mineral Deposits of South America, p. 294.

[3] Lycopodium, Equisetum, Aspidium, and Cyathea.

FORMATION OF NITRATES IN SOILS

By the oxidation of the organic matter in the soil, nitrates are formed, and in this process nitrifying bacteria play a very important rôle. These salts pass into the ground-water in moist regions, and are either washed away, or are used up by growing plants. In arid regions, on the other hand, these may accumulate to a considerable extent in the surface soil, or be concentrated in favorable localities.

The process of oxidizing the nitrogen of organic matter (ammonia, etc.) in the soil to nitrous acid, or the latter to nitric acid, is called *nitrification,* and the bacteria which accomplish this are called *nitrifiers.* Bacteria which accumulate the free nitrogen of the air on the roots of plants are called *nitrogen fixers.* The plants too (especially the legumes) which by the agency of bacteria form tubules on their roots, in which the nitrogen is fixed, are called *nitrogen fixing plants.* The breaking down of nitrates into nitrites, and nitrites into ammonia compounds, or the liberation of nitrogen from any of these is called *denitrification,* and the bacteria which accomplishes this are *denitrifiers.*

The nitrifying organism occurs in soil down to a limited depth. It also occurs in sewage and in river water, and is usually present in air or rain. In natural porous soil only nitrates are produced as the result of nitrification. In soil from which air is excluded by an excess of water, nitrites are produced but these are later converted to nitrates. Different bacteria may accomplish this. Nitrification appears not to be possible in the absence of phosphates, and it requires the presence of free oxygen in the soil. Experiments by Schloesing have shown that in soil holding 16 per cent. of water, a considerable amount of nitrification took place when 1.5 per cent. of oxygen was present in the atmosphere, but the rate of nitrification increased fourfold when 21 per cent. of oxygen was present. An increase in the proportion of water to 24 per cent. raised the rate of nitrification in atmospheres containing a small percentage of oxygen, the quantity of *dissolved* oxygen being thus increased.[1]

A base is necessary in the soil with which the nitrous and nitric acid produced can combine. Calcium carbonate generally present in soil, acts best for this purpose. The presence of more than a small amount of soluble alkali in the soil hinders nitrification. Nitrification occurs at temperatures as low as 3°C. but increases to a maximum at 37°C. decreasing rapidly above this, until beyond 55°C. there is no action. Drying of the soil even at low temperature is fatal to the nitrifying organism which it contains. If organic matter and denitrifying organisms are present, all nitrates present may be destroyed without injury to the nitrifying organism, however, which will resume its activity when favorable conditions are restored. The nitrifying bacteria are active when the soil is moist and aerated. Denitrification takes place when it is water logged.

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[1] Gale, *loc. cit.*, p. 31–33.

Nitrates are also produced from putrifying organic matter in contact with alkaline materials, such as lime or wood ashes, a process which has been used to some extent for the artificial production of saltpeter (Clarke). In northern India and Burma, potassium nitrate (Bengal saltpeter) forms abundantly in the soil around the cities and villages, where the decaying putrid matter is especially abundant.

GUANO AS A SOURCE OF NITROGEN

Guano is considered as one of the most important natural sources of nitrogen. Two kinds of guano are generally recognized: that formed from the droppings of sea birds along the rocky coasts selected for their resting places, and that formed from the droppings of bats in caves. Much nitrate or saltpeter is obtained in India and Ceylon from the excrements of bats in caverns or beneath overhanging cliffs.

Minerals in Guano Deposits.—A number of distinct mineral species have been detected in guano beds. The best known among these are:

Monetite—$HCaPO_4$
Bruschite—$HCaPO_4.2H_2O$
Metabruschite—$2HCaPO_4.3H_2O$
Martinite—$2H_2Ca_5(PO_4)_4.H_2O$
Callophanite—$Ca_3P_2O_8.H_2O$
Bobierrite—$Mg_3P_2O_8.2H_2O$
Newberyite—$HMgPO_4.3H_2O$
Hannayite—$Mg_3P_2O_8.2H_2NH_4PO_4.8H_2O$
Struvite—$NH_4MgPO_4.6H_2O$
Stercorite—$HNaNH_4PO_4.4H_2O$

Three of the more common minerals found in guano namely: Hannayite ($Mg_3P_2O_8.2H_2NH_4PO_4.8H_2O$), Struvite ($NH_4Mg$-

$PO_4.6H_2O$), and Stercorite ($HNaNH_4PO_4.4H_2O$), contain ammonium and from them and from ammoniacal dust derived from the guano beds, nitrogen may be obtained for the formation of nitrates in favorable localities. Ochsenius and Penrose believe that the nitrogen of the Chilean nitrate deposits was thus derived, such an origin having originally been suggested by C. G. Hillinger in 1860.

OCCURRENCE OF NITRATE DEPOSITS

Nitrate salts are found in all fertile soils but concentrated deposits occur only in extremely dry desert regions. Here they occur as bedded deposits in more or less impure mixture, known in South America as Caliche.

In addition to this type, nitrate salts also occur as incrustations in dry caverns and in crevices usually in limestone. They cover the surfaces of overhanging ledges in the caverns and may even coat stalactites and stalagmites.

The following are the principal nitrates found in nature, though others, containing nitrogen as ammonia are known.

Simple Salts:	
1. Soda niter (cubic niter)	$NaNO_3$
2. Saltpeter (niter)	KNO_3
3. Nitrobarite	$Ba(NO_3)_2$
4. Nitrocalcite	$Ca(NO_3)_2.nH_2O$
5. Nitromagnesite	$Mg(NO_3)_2.nH_2O$
Double Salts:	
6. Gerhardtite	$3Cu(OH)_2.Cu(NO_3)_2$
7. Darapskite	$NaNO_3.Na_2SO_4.H_2O$
8. Nitroglauberite	$6NaNO_3.2Na_2SO_4.3H_2O$

THE CHILEAN NITRATE DEPOSITS[1]

The Chilean deposits are the largest known nitrate deposits of the world. They occur in the deserts of Atacama and Tarapaca, which lie to the west of the Andes Mountains in the belt of the southern trades or southeasterly winds (18° to 30°S latitude). These winds "first lose a part of their moisture over the comparatively low Sierras of the east coast, where rainfall is over 80 inches a year. Then as they sweep over the Brazilian plains, the rainfall is less (between 40 and 80 inches per annum), to be increased again to over 80 inches as they rise in the Andes. After crossing the Andes, they descend, and being warmed both by compression during the descent and by contact with the warm surface of the lower region, they become drying winds with the

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[1] See *Miller, B. L.* and *Singewald, J. T.* The Mineral Deposits of South America, McGraw-Hill Book Co., 1919, pp. 283–301 and the bibliography cited on pp. 328–347. Also *Semper and Michels*, Die Salpeter Industrie Chiles, Zeitschrift für das Berg, Hütten, und Salinen-wesen im preussischen Staate, Bd. 52, 1904, pp. 359–482, London, 1905. Translation (La Industrie del Salitre en Chile) with einen dations in Publicado bajo la Vigilancia de la Sociedad Nacionel de Mineria, 418 pages, map; Santiago, 1908.

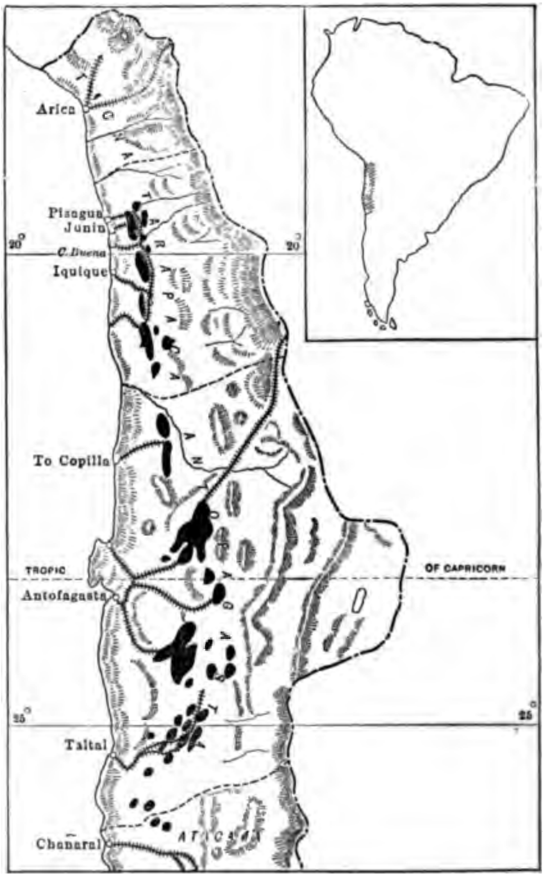

FIG. 98.—Sketch map of northern Chile showing approximate location of nitrate lands (black area). (*After Tower, from Miller & Singewald, Mineral Deposits of South America—McGraw-Hill Book Co.*)

result that the narrow Pacific coastal strip, to leeward of the Andes, is a pronounced desert from near the equator to about latitude 30°S "[1] (Fig. 98).

In the Atacama Desert the temperature in winter ranges from −12°C. (+10.4°F.) at 7 a.m. to +37°C. (+97.6°F.) at 11 a.m., and in summer from +5°C. to +55°C. (+41°F. to +131°F.).

Rain commonly falls here only at intervals of 3 or 4 years, and 8 or 10 years of unbroken draught are not unknown. So dry is the region that natural mummies are formed, one such of a copper miner having been preserved in a little altered form probably for hundreds of years.[2] The region has an elevation of 2,500 feet or more above the sea, and is a flat featureless pampas or plain bounded on the west by the coast ranges against which the surface of the pampas slopes from the higher Andes (Fig. 99).

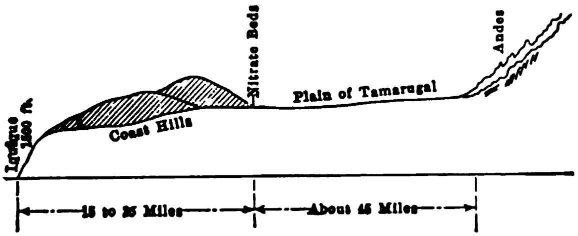

Fig. 99.—General east and west sections of the nitrate district of Chile; vertical scale greatly exaggerated. (*After Cueras from Miller & Singewald, Mineral Deposits of South America—McGraw-Hill Book Co.*)

The nitrate deposits are found in playas or "calicheras," the crude sodium nitrate being known as "caliche." They are located on the western or deeper margin of the plain near the coast ranges and in places upon the slopes of these ranges. They are found chiefly upon the margins of the salares or salines which occupy the desert depressions in this part of the plain. A characteristic section of such a calichera, 50 miles west of Talfal in the Atacama Desert, shows the following succession[3] in descending order.

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[1] Grabau, "Principles of Stratigraphy," p. 67.

[2] See "Principles of Stratigraphy," p. 1077.

[3] J. Buchanan, Jour. Soc. Chem. Ind., Vol. 12, 1893, p. 128.

B. Simmersbach and F. Mayer, Zeitschr. f. prakt. Geologie, 1904, p. 273. For variations see Miller and Singewald, *loc. cit.*, p. 289–291.

1. Sand and gravel	1–2 inches
2. "Chusca," a porous earthy gypsum	6 inches
3. A compact mass of earth and stones	2–10 feet
4. "Costra," a low-grade caliche containing much sodium chloride, feldspar and earthy matter	1–3 feet
5. "Caliche"	1½–2 feet
6. "Coba," a clay	±3 inches

The costra contains a considerable amount of bloedite ($MgSO_4.Na_2SO_4.4H_2O$), while the caliche contains the following minerals.

Anhydrite	$CaSO_4$
Gypsum	$CaSO_4.2H_2O$
Thenardite	Na_2SO_4
Mirabilite	$Na_2SO_4.10H_2O$
Bloedite	$MgSO_4.Na_2SO_4.4H_2O$
Epsomite	$MgSO_4.7H_2O$
Glauberite	$Na_2Ca(SO_4)_2$
Halite	$NaCl$
Darapskite	$NaNO_3.Na_2SO_4.H_2O$
Nitroglauberite	$6NaNO_3.2Na_2SO_4.3H_2O$
Lautarite	CaI_2O_6
Dietzeite	$7CaI_2O_6.8CaCrO_4$

In the following table from Penrose[1] a series of analyses of the caliche from different localities is given, showing the marked variability of the deposits.

TABLE LXXIX.—ANALYSES OF CHILEAN CALICHE

	1	2	3	4	5	6	7
$NaNO_3$	28.54	53.50	41.12	61.97	22.73	24.90	27.08
KNO_3	Trace	17.25	3.43	5.15	1.65	2.50	1.34
$NaCl$	17.20	21.28	3.58	27.55	41.90	24.50	8.95
$CaCl_2$	......	......	......	......	......	......	5.25
$MgCl_2$	......	......	......	......	......	......	0.18
$KClO_4$	Trace	0.78	0.75	0.21	Trace	Trace	Trace
Na_2SO_4	5.40	1.93	Trace	2.13	0.94	6.50	None
$MgSO_4$	3.43	1.35	10.05	0.15	3.13	6.50	None
$CaSO_4$	2.67	0.48	3.86	0.41	4.80	4.50	2.89
$Na_2B_4O_7$	0.49	0.56	0.20	0.43	0.53	0.15	0.52
NaI	0.047						
$NaIO_3$	0.043	0.01	0.05	0.94	0.07	0.054	0.08
NH_4 salts	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Na_2CrO_4	......	Trace	......	Trace	Trace		
Insoluble	40.30	2.07	31.86	0.39	22.50	28.40	47.34
H_2O combined, etc.	1.88	0.79	5.00	0.67	1.75	2.00	6.37
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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[1] R. A. F. Penrose, Jr., The Nitrate Deposits of Chile, Jour. Geol., Vol. 18, 1910, pp. 1–32(14). For other analyses, also for those of chusca, costra and coba, see Miller and Singewald, *loc. cit.*

The great variation in purity of the deposit is indicated by the percentages of insoluble material which ranges from 0.30 per cent. to 47.34 per cent. The amount of NaCl also varies greatly, being in one case more than half the soluble material. The perchlorate of potassium ($KClO_4$), usually present in small quantities, ranges in some cases as high as 6.70 per cent. It is regarded as an injurious constituent of the nitrates where these are required for agricultural purposes. In addition to the substances given in the table, there are always present some traces of rubidium and lithium.[1]

A thickness of the nitrate deposits of 1 to 1½ feet is common; of 2 to 3 feet less so, but not unusual; and of 4 to 6 feet very unusual. They are generally covered by a capping of sand, clay, gravel, and rock fragments from a few inches to 20 or even 30 or 40 feet in thickness, though in some cases only a few inches of desert dust cover them. The capping is called costra, and is generally more or less indurated with alternating harder and softer layers or patches. The covering material appears to be largely derived from the coast ranges. The average succession according to Penrose[2] is somewhat as follows:

'Chuca" (loose, wind-blown material, dust, sand and gravel, etc.)	0–several feet
"Costra" (capping of nitrate beds)	0–20 or even 30–40 feet
"Caliche" (crude nitrate)	0–6 feet
"Coba" (earthy floor of nitrate beds)	Indefinite, perhaps a few feet
Stratified sands, clays and gravels	To great depth

Sodium chloride is a common accompaniment of the nitrate deposits, and beds of salt of much greater extent than the nitrates are found in these pampas.

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[1] The following references are valuable for further detail in addition to those cited by Miller and Singewald.

V. L. Olivier, Annales chem. phys., 5th ser., Vol. 7, 1876, p. 289.

C. Ochsenius, Zeitschr. für prak. Geol., 1893, p. 217; 1901, p. 237; 1904, p. 242.

L. Darapsky, Das Department Taltal (Chile), Berlin, 1900.

A. Pessis, "Nitrates and Guano Deposits in the Desert of Atacama," London, 1878 (authority Chilean Government).

J. W. Flagg, Am. Chemist, Vol. 4, 1874, p. 403.

Semper and Michels, Zeitschr. Berg. Hütten und Salinen wesen, preuss Staat, 1904, pp. 350–482.

W. H. Ross, Pop. Sci. Monthly, Vol. 85, 1914, p. 134.

A. Gautier, Annales des Mines, 9th ser., Vol. 5, 1894, p. 50.

Ochsenius, C., Die Bildung des Natron Saltpeters aus Mutterlangensalzen, Stuttgart, 1887.

[2] Penrose, *loc. cit.*, p. 12. See also Miller and Singewald, *loc. cit.*, p. 289.

The calicheras of the Pampa de Tamarugal in the Atacama Desert (near Iquique), lie about 3,000 feet above the sea, between the Andes or High Cordilleras, and the coastal ranges.[1]

The plains or pampas are about 30 or 40 miles wide, with a very gradual downward slope to the west, where they are shut in by the coast line of hills which lie parallel to the High Cordilleras. This coastal range forms a boundary to the waters from the western side of the Cordilleras. These waters cover the plains for a short time every seven or eight years, when the tropical rains in the High Cordilleras are exceptionally heavy. Newton holds that the waters dissolve the nitrates which have been forming during the intervening dry periods in thousands of square miles of the porous soil of the pampas by the oxidation of organic matter and the nitrifying action of bacteria. Gathering along the eastern or landward side of this coastal range they evaporate some thirty miles from the sea, and at the lowest point about 2,500 feet above the sea level. Here the nitrate deposits are found.

The caliche of this Pampas varies from 4 to 12 feet in thickness. Bromides are absent and only traces of phosphates occur. These deposits were considered by Darwin as of marine origin, but the fossils he refers to as occurring with them are, as Newton points out, derived from the Cretacic beds which in one or two places are found in contact with the caliche. The probability that the nitrates of this region were derived from guano is very slight, since the region is so high above sea level, and since phosphates are practically absent. Occasionally the remains of birds are found in the deposits, but they are of species now living in the region, and they and their guano are of only sporadic occurrence.

The nitrate deposits of the Barateras de Maricunga, south of the Atacama Desert (about latitude 27°S), are remarkable in that they lie in a mountain valley at an elevation of 3,800 meters above sea level,[2] and at a distance of about 180 kilometers from the coast. Their origin is essentially similar to that of the nitrates of the Atacama Desert region.

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[1] W. Newton, Jour. Soc. Chem. Ind., Vol. 19, 1900, p. 408. Ibid., The Origin of Nitrates in Chile, Geol. Mag., 1896, pp. 339–342.

[2] E. Semper and M. Blanckenhorn, Zeitschr. für prakt. Geologie, 1903, p. 309.

The origin of the Chilean nitrates has been explained in the various ways already outlined. Miller and Singewald comment on this: "There is no evidence to show that any one of the possible sources would be adequate to account for all the nitrate and we believe that all combined would be inadequate, if it were not for the all important remarkable conditions of climate, underground waters, and geological structure existing in the region"[1] and they rightly hold that the emphasis should be laid upon the physical characteristics of the region as more fundamental than the mode of generation of the nitrates.

OTHER NITRATE DEPOSITS OF SOUTH AMERICA

Argentina.—In the Province of Jujuy, in northern Argentine and within the Andean Chain, occurs a playa known as Salina Grandes, about 480 km. from the coast (latitude 23°S), and lying at an elevation of 3,500 meters above the sea and between mountain chains rising about 6,000 meters above the sea.[2] The center of the deposit in the playa is covered with rock salt 20 to 30 centimeters in thickness, around the border of which ulexite nodules are distributed in an uneven manner. The borax minerals found are:

Colemanite	$2CaO.3Bo_2O_3.5H_2O$
Priceite	$3CaO.4Bo_2O_5.6H_2O$
Bechilite	$CaO.2Bo_2O_3.4H_2O$
Hayesine	$CaO.2Bo_2O_3.6H_2O$
Ulexite	$Na_2O.2CaO.5Bo_2O_3.16H_2O$

Gypsum is abundant, and glauberite, pickeringite, and soda niter occur. The locality is flooded in spring by waters from the mountains, but is dry in summer. The boric acid is believed to be of volcanic origin.

Another and larger Salina Grandes lies in the province of Santiago del Estero and in adjoining provinces, in West Central Argentine, east of the Andean chain and between it and the Sierra de Cordoba at an elevation of 196 meters above sea level.

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[1] *Loc. cit.* p. 296.

[2] H. Buttgenbach, Gisements de borate des "Salinas Grandes" de la Republique Argentine, Annales Soc. Geol. Belgique, Vol. 28-M, 1900-1901, pp. M 99–M 116.

This lies across latitude 30°S and comes alternately under the influence of the easterlies and the westerlies as they shift north and south with the seasons.[1] Crusts of salt are formed during the summer, while the center of the lagoon contains a mother liquor from which sodium nitrate is obtained.

Colombia.—A deposit of sodium nitrate has been described from the valley of the San Sebastiano River in Colombia.[2] The sodium nitrate deposit is from ½ to 3 meters thick and is underlain by a bed consisting of a mixture of gypsum and calcareous clay, and containing some oxide of iron and common salt.

Analyses of two samples gave the following:

TABLE LXXX.—ANALYSES OF COLOMBIAN NITRATES

	Pure deposit, sp. gr. 2.01	Average dried sample
$NaNO_3$	23.1	11.4
$CaCO_3$	....	32.5
$CaSO_4$	8.5	20.1
$NaCl$	34.1	
$Al_2(SO_4)_3$	3.4	
$Ca_3(PO_4)_2$	....	2.5
SiO_2	24.7	32.4
MgO	Trace	
Fe_2O_3	....	Trace
Organic matter	....	1.0
H_2O	5.5	
Total	99.3	99.9

The Nitrate Deposits of Cochabamba, Bolivia.—These deposits are of importance because they consist in large part of potassium nitrate.[3] They lie within the Cordillera Real, at an elevation of over 2,000 m. above the sea. These deposits are associated with borax, which also occurs in the soil below the nitrate layer. An analysis of a sample of the niter gave Sacc the following composition.

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[1] W. F. Reid, Jour. Soc. Chem. Ind., Vol. 19, 1900, p. 414.

[2] Zaracristi, Bulletin du Bureau des republiques Americaines, Dec., 1893 reviewed in Berg und Hüttenmännische Zeitung, Vol. 55, 1896, p. 391.

[3] F. Sacc, Compt. Rend., Vol. 94, 1884, p. 84.

TABLE LXXXI.—ANALYSIS OF BOLIVIAN NITER

KNO_3	60.70
$Na_2B_4O_7$	30.70
$NaCl$	Trace
H_2O	Trace
Organic matter	8.60
	100.00

The nitrate is attributed by Sacc to the oxidation of ammonium salts in the soil.

NITRATE DEPOSITS IN THE UNITED STATES[1]

Eastern United States.—Nitrate deposits have long been known to occur in a number of limestone caves in the eastern United States. The source of the niter is generally the guano of bats. Those deposits recorded are:

Alabama, Niter, (KNO_3), in limestone caves; mined during the Civil War.

Arkansas, Niter (KNO_3), in Marion and Newton Counties in limestone caves.

Illinois, Niter (KNO_3), in caves in Harrison and Crawford Counties.

Indiana, Niter (KNO_3), or niter earth, in Wyandotte Cave and Saltpeter Cave, Crawford County, and Saltpeter Cave, Wyoming Co.

Kentucky, Niter (KNO_3), in Mammoth Cave, Edmonson County, and in many other limestone caves in the southern and central parts of the state.

Missouri, Niter (KNO_3), in Magnesian limestone caves in Pulaski, Maries, Calloway, and Ozark Counties.

North Carolina, Niter (KNO_3), as crystalline crusts on mica slate on Nantahala River in Cherokee County.

Tennessee, Niter (KNO_3), reported in many limestone caves, especially in the Cumberland tableland, not of much account.

West Virginia, Niter (KNO_3), or "Peterdirt" in caverns in Greenbrier, Monroe, and Pocahontas Counties.

During the war with England in 1812 the niter of Wyandotte

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[1] See Hoyt S. Gale, Nitrate Deposits, Bull. U.S.G.S. 523, 1912, where detailed references are given.

Cave, Indiana, and of the Kentucky caves, was used in the manufacture of gun-powder. The name Indiana Saltpeter Cave was given to the "Old Cave" or only part of Wyandotte Cave then known.

Analyses of the Bat guano from Wyandotte Cave gave the following results.

TABLE LXXXII.—ANALYSIS OF BAT GUANO FROM WYANDOTTE CAVE, INDIANA

Loss at red heat	44.10
Organic matter	4.90
Ammonia (NH_4)	4.25
Silica (SiO_2)	6.13
Alumina (Al_2O_3)	14.30
Ferric oxide (Fe_2O_3)	1.20
Lime (CaO)	7.90
Magnesia (MgO)	1.11
Sulphuric acid (H_2SO_4)	5.21
Carbonic acid (CO_2)	3.77
Phosphoric acid (P_2O_5)	1.21
Chloride of alkalies and loss	5.87
	100.00

Western United States.—Nitrate deposits have been observed in a number of places in the western United States.

Arizona.—Gerhardtite (nitrate of copper) occurs in the Clifton Morenci district in cliffs of granite porphyry in Chase Creek Canyon. According to Lindgren this was formed by trickling of atmospheric waters over and through rock containing a small percentage of copper. The same mineral is also found in copper mines at Jerome, Arizona.

Niter (KNO_3) is frequently found on old walls in ancient cliff-dwellings of Walnut Canyon, and on the overhanging limestone shelves. Nitrocalcite ($Ca(NO_3)_2nH_2O$) is also formed by reaction between the lime carbonate and bat guano or other organic sources of Nitrogen. Veins of nitrocalcite occur in Mississippic limestones on Gila River.

California.[1]—Soda niter ($NaNO_3$) occurs in San Bernardino County and as crystals lining a cave in the Calico District. Potash niter (KNO_3) occurs in the deserts northeast of Salton, Riverside County. Niter-bearing earths of low grade occur in extensive deposits in Inyo County along the lower valley of Amargosa River, above the south end of Death Valley and on the Colorado River between the Needles and Yuma. They average generally less than 1 or 2 per cent. of nitrate salts. They are supposed to be formed by activities of bacteria on organic material and brought to the surface in solution by capillarity and by evaporation in the dry climate are left as nitrate-bearing saline crusts (Gilbert Bailey). The soil of an alkali tract on Merced River, lying in a local basin of impervious limestone, carries nitrates in exceptional abundance. The following table gives an analysis of this soil (*A*), and of the soluble salts in an alkali crust near Tulare City (*B*) (Hilgard).

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[1] See also Ochsenius, Natron Saltpeter in California, Zeitschrift f. prakt. Geol., 1902, p. 337.

TABLE LXXXIII.—COMPOSITION OF NITRATE-BEARING SALTS FROM MERCED BOTTOM, MERCED COUNTY, CALIFORNIA (A), AND FROM SAN JOAQUIN VALLEY, NEAR TULARE CITY, CALIFORNIA (B)

	A	*B*
Soluble salts in 100 parts of soil crust	1.00	
Sodium sulphate (Glauber salt)	3.88	20.91
Sodium nitrate	10.72	16.40
Sodium carbonate (sal soda)	63.00	27.02
Sodium chloride (common salt)	1.21	12.21
Sodium phosphate	4.10	1.87
Potassium sulphate	.....	3.25
Ammonium carbonate	.....	1.27
Organic matter	.....	17.07
	82.91	100.00

Niter is also reported from Pilot, on an old beach line above Searles Lake, from the playa deposits of Danby Lake, and from an old shoreline above Salton Sea (Volcano).

Colorado.—Nitrate-bearing soils similar to those of southern California are found in several places in Colorado. The areas are characterized by a brown color on the surface and appear oily or wet, sometimes glistening and barren of vegetation, the excess of nitrates being injurious to plant life. Analysis shows some of the air-dried soil 2 inches below the surface to contain 6.5 per cent. of nitrates. According to W. P. Headden[1] there are hundreds of acres of land in Colorado which carry from 1 to 5 tons of nitrates in the top 2 inches of soil. These lie at altitudes of 3,300 to 7,500 feet above the sea. Experiments on these soils have given a maximum result in 27 days corresponding to the fixation of 5,616 pounds of nitrogen per acre-foot per annum, or 17.5 tons of proteids. Experiments in nitrification have shown that "the maximum increase obtained in 48 days was 138 per cent. of the nitric nitrogen present at the beginning of the experiment, which corresponded to the formation of 5 tons of sodic nitrate per acre-foot, or 4,000,000 pounds of soil per annum."[1]

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[1] Proc. Col. Sci. Soc., Vol. 11, 1911, pp. 99-122.

Idaho.—Niter salts of small extent and believed to be of cave origin are reported from near Soda Springs and Pocatello, Banneck County, from Blaine County, from the neighborhood of the Utah-Nevada line, and from Wayne County in central Idaho. The crude nitrate from a cavern in red sandstone 35 miles northeast of Soda Springs gave the following analysis.

TABLE LXXXIV.—COMPOSITION OF CRUDE NITRATE FROM IDAHO

	1	2
Residue insoluble in H_2O	4.22	2.73
Nitric nitrogen	11.12	11.48
Ammoniacal nitrogen	None	None
Calcium	2.91	2.12
Magnesium	0.11	0.17
Potassium	30.89	31.55
Sulphur	1.54	1.58
Chloride	Trace	None
	50.79	49.63

Other deposits occur in the Homedale region of western Idaho and eastern Oregon, lying chiefly in the latter state. They will be discussed with other deposits of that state.

New Mexico.—Nitrate of soda is reported from the extreme southeastern portion, and the adjoining portions of Chihuahua, Mexico. It is deposited by springs and appears to be in considerable quantity. Nitrate salts are also reported from other parts of the state.

Nevada.—Near Lovelock on the western slope of the Humboldt Range, Nevada, above Humboldt Lake, and southwest of Lovelock, occur a number of nitrate deposits consisting of incrustations on the under side of projecting ledges of rhyolite. Some of these incrustations are chiefly, if not wholly, sodium chloride or sulphate, but in several cases nitrates abound. Analyses of two of these are given in the subjoined table. The deposit has been regarded as formed from bird guano deposited here, when this region was a part of the shores of Lake Lahonton. Near Gerlach, Washoe County, in the northern part of the Granite Range occurs an almost pure deposit of potassium nitrate under ledges and in cave-like cliff formations in a canyon. It occurs as a white crystalline salt in crevices and concentrated in veins in the slide rock at the base of the cliff, partly or wholly in positions protected from leaching by rain, snow, or surface waters. The NO_3 in these salts varies in different samples from a mere trace to over 50 per cent. of the material. The quantity seems, however, to be limited and its source is regarded as being probably bat guano, which is still being deposited on these overhanging ledges. Analyses of the purest salts are given in the table.

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[1] Headden, *loc. cit.*

TABLE LXXXV.—ANALYSES OF GUANO AND OF NITRATE SALTS FROM LOVELOCK (B, C) AND GERLACH (D, E) NEVADA AND FROM UTAH

	A	B	C	D	E	F Greenwich Canyon, Utah
	Guano	Lovelock, Nev.		Gerlach, Nev.		
Insoluble in H_2O	34.10	30.89	4.00	10.04	14.58	46.04
NO_3	Trace	35.65	53.12	52.40	50.42	28.53
Na	0.67	20.20	26.26	1.07	1.28	0.18
K	5.45	Trace	Trace	33.61	31.42	19.18
Cl	3.18	10.90	8.83	Trace	Trace	0.20
SO_3	.....	Trace	1.33	Small	.....	Small
P_2O_5	0.64					
CaO	......	Very little	0.53	Small	Small	Small
	44.06	97.64	94.27	97.12	97.70	94.14

The guano given in the first column lost about 49 per cent. on ignition. The Cl determination is only approximate.

The Lovelock deposits are thus mostly soda niter, while those near Gerlach are potassium niter or saltpeter. Gale suggests that the sodium base of the former may have been supplied by the waters of former Lake Lahonton, while the potash base of the Gerlach region was supplied by the brecciated acidic lava of that region, which is rich in potash-bearing minerals.

Oregon.—In the valley of Sucker Creek, eastern Oregon, and along Jump Creek in the vicinity of Homedale, southern Idaho, nitrate deposits have been found in localities similar to those of Nevada, and essentially of similar origin though the evidence of occupancy of the caverns by bats is less clear. The rhyolites here are fissured and have a shelly structure, and the mineral occurs in veinlets in these fissures. It also tends to accumulate in the border zone between the soil and the bases of the cliffs, where it is sometimes plentiful enough to be shoveled into buckets. Common salt and sodium sulphate are associated with these nitrates in certain localities. Various combinations of salts have been found, some of which are as follows:

$NaNO_3$ and Na_2SO_4
$NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$
$NaCl$, KNO_3, some $Ca(NO_3)$ and Na_2SO_4.

Some of the deposits contain no nitrates but are combinations of $MgSO_4$ and Na_2SO_4, with or without $NaCl$. In one sample (Abbie Claim) the percentage of NO_3 was 59.91, of the soluble salt with both potassium and sodium as bases. In another sample (Dorothy Claim) the NO_3 was 47.25 per cent. of the soluble salt with sodium as the chief base.[1]

Texas.—Nitrate of soda, possibly similar to those deposits of New Mexico and Chihuahua, Mexico, occur in Presidio County, Texas. Potassium niter has also been reported from El Paso County and from caves elsewhere in the state.

Utah.—Deposits of potassium niter, essentially similar to those found at Gerlach, Nevada, are found in Greenwich Canyon, Piute County, Utah. They occur in veins and incrustations on the underside of ledges of brecciated rhyolite, in regions now inhabited by bats, whose guano is believed to have furnished the nitrogen. The quantity is restricted in location and limited in amount. Analysis of the best material is given in column *F* of Table LXXXV.

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[1] For a full discussion of these deposits see G. R. Mansfield, Nitrate Deposits in Southern Idaho and Eastern Oregon, Bull. U. S. Geol. Surv. 620-B, pp. 17–44, 1915.

Wyoming.—Nitrate of potash was found in the Leucite Hills of Wyoming in a crevice in the lavas of which these hills are composed. The deposit "seemed to occur as a partial crust to the cavity and as a filling for irregular fissures which extended downward and backward into the body of the rock."[1] The location was "fully exposed to the prevalent northwesterly breeze, and rain could penetrate to the inner wall only when driven by very strong winds." The mineral was a rather coarse, granular aggregate with the following composition.

TABLE LXXXVI.—ANALYSIS OF NITER FROM WYOMING

K_2O	44.91	96.40 niter
N_2O_5	51.49	
CaO	1.09	3.31 gypsum
SO_3	1.59	
H_2O	0.63	
Na	0.07	0.16 halite
Cl	0.09	
	99.87	

A soda niter was also noted in some places as a scanty white coating on protected rock faces. This had the following composition.

TABLE LXXXVII.—COMPOSITION OF SODA NITER FROM WYOMING

$NaNO_3$	87.98
KNO_3	10.66
$CaSO_4.2H_2O$	0.71
H_2O	0.54
Cl	Trace
	99.89

Cross suggests the possibility of a fumarolic origin for these deposits, but does not deny the possibility that they may have been derived by percolating waters from organic matter (guano) of birds or other small animals which inhabited clefts above the deposit.

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[1] Whitman Cross, Am. Jour. Sci., 4th ser., Vol. 4, 1897, pp. 115–141.

CHAPTER XIV

THE OCCURRENCE AND ORIGIN OF DEPOSITS OF PHOSPHATE OF LIME

Classification of Lime Phosphates According to Mineral Character.—The deposits of phosphate of lime in nature have been classed as follows:[1]

- **A. Mineral Phosphates.**
  - 1. *Apatites.*
    - *a.* Fluor-apatites.
    - *b.* Chlor-apatites.
  - 2. *Phosphorites.*
- **B. Rock Phosphates.**
  - 3. *Amorphous nodular phosphates.*
    - *a.* Loose nodules.
    - *b.* Cemented nodules or conglomerates.
  - 4. *Phosphatic limestone beds.*
  - 5. *Guano.*
    - *a.* Soluble Guano.
    - *b.* Leached Guano.
  - 6. *Bone beds.*

OCCURRENCE OF PHOSPHATE DEPOSITS

A. Mineral Phosphates

The mineral phosphates are characterized by definiteness of chemical composition and physical characters of mineral species, or at least show a strong tendency in this direction. Their fullest mineral expression is found in crystalline apatite.

1. Apatites ($Ca_3O_8P_2 + \frac{1}{3}(Cl_2F_2)$ Dana).—This is the crystalline form of lime phosphate, in which chlorine and fluorine are present in varying proportions, according to the preponderance of which we have either fluor- or chlor-apatites.

Apatite is most common in crystalline rocks, but is also found in metamorphic sediments, and occasionally as small crystals in other phosphate deposits. The Canadian apatite has been regarded by Dawson as originally derived from organic deposits, but T. Sterry Hunt believed it to be of non-organic (chemical) origin. Some of it seems to have an eruptive origin, a source generally held for the Norwegian apatites. (For further detail see under Pre-Cambric (Vol. II).)

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[1] R. A. F. Penrose, Jr., Nature and Origin of Deposits of Phosphate of Lime, Bull. U. S. Geol. Survey, No. 46, 1888.

2. **Phosphorites.**—This name is applied to the fibrous concretionary and partly scaly, phosphate of lime deposits as well as the vitreous and earthy varieties associated with them and grading into them. They occur in several ways. (*a*) In hollows or caverns in limestone dolomite or other rock. They may be open to the surface or covered by residual or other clay. To this group belong the phosphorites of Nassau of northwest Germany which occur in hollows in Devonic limestone, the "Bordeaux Phosphates" which occur in the Jurassic limestone of southwest France, portions of the Florida phosphates, and others. The Nassau phosphorites are believed to be derived from the concentration of phosphatic material from the organisms of the rocks, but the history of the Bordeaux phosphates is more in doubt. They have been regarded as the result of leaching of bones, Guano, etc., deposited in the fissures and caverns of the Jurassic limestone in Tertiary time, through rising vapors, through the action of springs, etc.

(*b*) As veins along the contact of igneous and sedimentary rocks or in veins or rocks of quartz and calcite cutting slates or other country rock, and apparently deposited by rising mineral waters or gases. To this group belong the phosphorites of the province of Estremadura, Spain, of Siluric or older age. (For further discussion of these deposits see the respective chapters in Vol. II.)

B. Rock Phosphates

The rock phosphates have no definite chemical composition and lack the homogeneous nature and other fixed characteristics of a true mineral (Penrose).

3. **Amorphous Nodular Phosphates.**—These consist generally of calcareous matter more or less completely phosphatized and occur either as loose nodules in a matrix of variable composition or as a conglomerate in which the pebbles are phosphate of lime and the matrix is of a calcareous phosphatic, siliceous or ferruginous nature (Penrose). To this group belong the Ordovicic phosphates of North Wales, and possibly those of Tennessee,

the Jurassic and Cretacic phosphates of England and of Russia, and the Cretacic phosphates of Belgium, of northern, central and eastern France and of Russia, and the Tertiary phosphates of England, North and South Carolina, Alabama, Martha's Vineyard and a part of those of Florida and those along the Cretacic-Tertiary boundary in Tunis and Algeria, North Africa. They are fully discussed under their respective enclosing formations in Vol. II.

These are probably all of organic origin, representing either the deposition of highly phosphatic material at a given zone, or what is probably more frequent, the concentration through weathering on exposure of the upper portion of a formation through which these nodules were originally scattered, and subsequent covering by later deposits either of the same or a younger system. Such beds of phosphates therefore often if not always mark a hiatus between the enclosing beds and a period of land during their concentration. They may however indicate a period of non-deposition of other material than the phosphatic bones, teeth and excrements of marine organisms in relatively deep water, and so indicate rather a break in the rhythm of sedimentation of the type recently designated a diastem by Barrell[1] instead of a disconformity or unconformity.

4. Phosphatic Limestone and Other Beds.—These comprise ordinary sedimentary limestones which contain considerable quantities of phosphate of lime, either as an original deposit of phosphatic material or due to phosphatization during deposition of certain parts of the series by sedimentation in waters charged with phosphate in solution. Shales may in a similar manner be charged with phosphate of lime.

To this group belong certain Ordovicic limestones of Kentucky and the Permic phosphate deposits of Wyoming and Idaho. Limestones of this type but carrying only about 12 per cent. of phosphate of lime are recorded from Russia. The Kentucky limestones carry 31.8 per cent. of this substance while the Wyoming and Idaho deposits range up to 36.8 per cent. of P_2O_5. The upper Vicksburg limestone of Florida has also been phosphatized in this manner as has also part of the Alum Bluff formation. Ledoux[2] cites a recent case of phosphatization of limestone by the leaching of overlying guano beds from the south Pacific Islands.

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[1] Bull. Geol. Soc. Am., Vol. 28, p. 794, 1917.

[2] Albert R. Ledoux, N. Y. Acad. Sci., Trans., IX, pp. 84–94, 1890.

Here the limestone has been phosphatized to the depth of several feet, within a period of twenty years.

5. Guano.—This is formed chiefly from the excrements of birds, especially those which inhabit isolated islands and promontories of the sea coast. Excrements of bats in caves or under overhanging ledges, likewise form guano deposits which moreover are important sources of nitrates. On low sea coasts the droppings of seals and other marine mammals become another source of guano, as in certain places on the coast of Tarapaca in Chile. These often contain smooth fragments of porphyry from 3 to 10 cm. in length derived from the stomach contents of the seals.

6. Bone Beds.—Phosphate deposits consisting largely of bones occur in caverns especially such where carnivorous animals dragged their prey, and where they sometimes form beds of osseous breccia many feet in thickness. They are most common in European caves, but they also occur about the swampy margins of salt licks, as at Big Bone Lick in Kentucky, in the Mauvaises Terres of Nebraska and elsewhere in America as well as in Europe. None of these deposits are as a rule very extensive. Bone heaps may also result from the sweeping together by floods of herds of animals suddenly overwhelmed or killed by previous drought as in the case of the great drought ("gran seco") of 1827 to 1830 in Buenos Aires, where as Darwin has described "the cattle in herds of thousands rushed into the Paraña, and being exhausted by hunger they were unable to crawl up the muddy banks and thus were drowned." Several hundred thousand animals thus perished, and were swept into the estuary of the Plata. Vast numbers died by drinking the saline waters of the rivers and their bones were buried by the floods of the succeeding rainy period.

Bone beds consisting largely of fish remains have been formed in the past, where an invasion of the sea water into the estuaries killed the stenohaline river fish. Such bone beds are found especially in the Siluric of Europe and the Devonic of North America. They are seldom of great thickness but often of considerable extent.

CLASSIFICATION OF PHOSPHATE DEPOSITS ACCORDING TO ORIGIN

Deposits of phosphate of lime may be classed either as original or secondary. The former when occurring in the stratified formations are primarily derived from organic sources, and consist of the bones, teeth or excrements of vertebrate animals or the phosphatic shells of brachiopods, mollusks, crustaceans and other invertebrates. The secondary phosphates are probably in large part derived from this group by leaching or solution, and redeposition, either by circulating waters or by steam or gases. Redeposition may be direct in cavities, or around other bodies, etc., or may result in replacement of the carbonic acid of the carbonate of lime or other substances by phosphoric acids. Phosphate of lime is also held by many to be formed from inorganic sources. This is held especially for the apatite which occurs in many igneous and metamorphic rocks. These may be primary deposits or they may be of secondary origin in metamorphism.

Phosphates of Organic Origin

Phosphates of organic origin are formed as contemporaneous deposits in the stratified rocks and represent beds of phosphatic fossils. According to place of formation they may be regarded either as marine or continental, according to their history they may further be undisturbed or concentrated. Either type of deposit may of course suffer alteration, as in the leaching of guano-beds, and the enlargement of teeth, bones, etc. by addition of secondary phosphatic material. For purposes of clear conception it is desirable that the pure types be separately discussed though they may seldom be found in their original condition in nature.

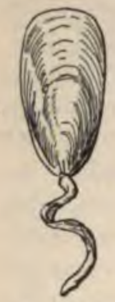

FIG. 100.—*Lingula pyramidata* (natural size), drawn from a specimen by Mary Welleck.

Marine Organic Phosphate Depositr.—It is fortunate that deposits of this type are accumulating today in many portions of the oceans and that they have been made the subject of study by deep sea expeditions. We may readily distinguish the following groups. (1) Organic phosphate scattered through the stratified series of normal marine deposits, such as the shells of the brachiopod *Lingula*, a species of which (*Lingula pyramidata*, Fig. 100) now living along the Atlantic Coast of the northern United States, contains about 55 per cent. of lime and magnesium phosphate, while a Cambric *Obolus* shell has yielded 36.54% P_2O_5 and the exoskeletons of crustaceans carry up to 26% $C_3P_2O_8$.[1] Other sources of phosphoric acid are the teeth of

[1] Lindgren, W., Mineral Deposits, 2nd ed., 1919, p. 279, McGraw-Hill Book Co.

fishes, etc. (2) Deposits of phosphatic young shell stages which on sinking to the bottom are killed in the stagnant water. Thus only the young stages accumulate often in vast quantities, forming with other pelagic young, the only common fossils of the sediment. Such young gastropod protoconchs, known as *Spirialis* occurs in vast numbers in certain Tertiary beds of the Crimo-Caucasian region, and others, known as *Cyclora* abound in the Ordovicic rocks of Tennessee. These latter by concentration have produced some of the important phosphate deposits of that state. (3) Deposits of bones, teeth and excrements of marine animals in deeper waters where clastic sedimentation is slight and where an opportunity for partial decomposition of the organic matter and the formation of phosphatic nodules is furnished. These are the common types of phosphate deposits in the modern sea.

The living marine organisms extract the phosphoric acid from the sea water and deposit it as phosphate of lime in their hard structures. The amount of phosphoric oxide (PO_4) in ocean water is so slight that it is not generally given in analyses, constituting together with the iron (Fe) and silica (SiO_2) less than one-tenth of 1% (0.02–0.08 %) of the total saline content which, it will be recalled is itself only about 35 grams for every liter of ocean water. Thus the three substances together form only from 0.007 to 0.028 permille of the saline content of the sea water. Nevertheless on the basis of the mean of this or 0.0175 permille, a cubic mile of sea water would contain roughly, 3,750 short tons of these substances or in very round numbers there may be a thousand tons of PO_4 in every cubic mile of sea water.

Concentration of phosphate of lime occurs in many places at the bottom of the modern Atlantic. Between Cape Hatteras and lat. 31° 4′ N "phosphate of lime and manganese concretions are present in all the deposits, and one remarkable concretion of these substances [was obtained] in a depth of 333 fathoms, immediately under the waters of the Gulf Stream."[1]

Concretions of calcium phosphate, were very numerous in the deposits dredged by the Blake from the Gulf of Mexico and the Florida Straits. A fragment of bone with the structure perfectly preserved was obtained in 125 fathoms southwest of Land Key, Fla., and this carried 33.42 per cent. of P_2O_5.

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[1] Murray, J., Report on the Specimens of Bottom Deposits, Harvard College Mus. Comp. Zool. Bulletin, Vol. 12, p. 41, 1885.

"At the same place and depth there was a concretion of a brown color, consisting of an aggregation of calcareous organisms cemented by a brownish yellow matter often showing concentric rings after the manner of agate. This yellowish brown matter is isotropic; between crossed nicols only the Foraminifera calcite and the shells of the Foraminifera brighten up; the calcite lies crystallized in the interior of the Foraminifera."[1] Chemical treatment of the yellowish brown matter gave reaction for phosphoric acid. The phosphate nodules from the American coast were formed at depths of 125 fathoms or more. Murray states that whereas the percentage of phosphate of lime is usually small in deep-sea deposits, it increases in some places. The concretions of this substance, he says, appear always to be associated in an intimate way with organisms. Concerning this matter, he says in the Report on the Deep Sea Deposits Dredged by the Challenger (p. 396). "It may be pointed out that phosphatic nodules are apparently more abundant in the deposits along the coasts where there are great and rapid changes of temperature, arising from the meeting of warm and cold currents, as for instance off the Cape of Good Hope and off the eastern coast of North America. It seems highly probable that in these places large numbers of pelagic organisms are frequently killed by these changes of temperature, and may in some instances form a considerable layer of decomposing matter on the bottom of the ocean."

A significant fact, to be kept in mind in the interpretation of older phosphatic nodules is the almost constant presence of Foraminifera shells in the deep sea phosphate nodules. The mode of formation of the concretions on the ocean floor is not well understood. Murray says: "It may be supposed that this phosphatic matter dissolved in the sea water impregnating the mud, is endowed with the properties of colloidal bodies, for we know that phosphate of lime presents incontestable analogies with certain colloids, for example, with hydrated silica. By admitting that phosphate of lime can affect this colloidal state, it is sufficient that a center of concretion should arise to initiate precipitation, and the nucleus once formed would subsequently enlarge by successive additions.

"Many substances may have played, with respect to the phosphate, the rôle of center of attraction. It may have originated in the first instances as we have shown in the filling up of the hollow spaces of a Globigerina shell, afterward it may be deposited around this shell and agglutinate the surrounding portions of this deposit into a more or less compact mass. The organic remains at the bottom of the sea often retain for a long time some of their sarcodic substances, and we are inclined to think that this exercises upon the phosphate an attraction which might be considered as a feeble echo of that exercised by living matter. This view might be supported by recalling the frequent incrustations of phosphate and its concretionary development upon the remains of plants and animals. At the same time it must be pointed out that phosphate of lime is sometimes formed around inert matters to which no affinity would appear to carry it. A solid body of any kind appears to serve as a nucleus, though phosphatic nodules are by preference formed around organic centers, but whatever the nature of the nucleus once the first layer of the concretionary substance is deposited, it no longer remains inert, acting in its turn as a center of attraction and grouping around it just as the solvents furnish material, all the molecules of the same nature which are found within its radius of attraction."[1] Analysis of phosphate nodules from the sea bottom at 150 fathoms *A* and 1,900 fathoms *B* gave the following composition.

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[1] Murray, Ibid., p. 52–53.

TABLE LXXXVIII.—COMPOSITION OF PHOSPHATIC NODULES FROM THE SEA BOTTOM

	A	*B*
P_2O_5	19.96	23.54
CO_2	12.05	10.64
SO_3	1.37	1.39
SiO_2	1.36	2.56
CaO	39.41	40.95
MgO	0.67	0.83
Fe_2O_3	2.54	2.79
Al_2O_3	1.19	1.43
Loss on ignition	Undet.	3.65
Insoluble residue[2]	17.34	11.93
Total	95.89	99.71

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[1] Murray, Sir John, *loc. cit.*, pp. 52–53.

[2] Consisting of $SiO_2.Al_2O_3.Fe_2O_3$, CaO and MgO.

Many older beds of phosphate nodules in the stratigraphic series have been interpreted as formed in a manner analogous to the modern deep water nodules of the ocean. Among these are especially the nodular beds of the Jurassic and Cretacic of England and other parts of Europe, and many Tertiary occurrences. Among the latter are the phosphatic nodules of the Alum Bluff formation of Florida, which are generally regarded as the source of the phosphoric acid of the extensive secondary phosphate deposits of the region.

It may be well to note in passing however that not all of the deposits thus interpreted can be accepted as of such simple origin. Indeed, beds of phosphate nodules which exactly reproduce the modern deposits are extremely rare if not actually unknown. Nor are the characters of the strata always consistent with the requirements of origin in water 125 fathoms (750 feet) or more in depth. Indeed the characters of the Alum Bluff formation, the nodules of which are cited as good examples of marine phosphate deposits indicate that the depth of the water "was probably in no place over 100 feet."[1]

Concentration of Phosphate Nodules and Granules of Marine Origin

When a bed of limestone rich in the remains of organisms in the shells or other structures of which phosphoric acid is a notable constituent, becomes subject to attack by the atmosphere on exposure as a land surface, the carbonate of lime may be removed by solution, while the phosphate which is almost insoluble except if an excess of CO_2 is present, remains behind. In this manner a concentration of the phosphatic organic remains takes place and these by subsequent alteration, and by the redeposition of such phosphate as is dissolved may form phosphorites or beds of phosphate nodules, etc.

It will be noted first that the rocks in question must be exposed to the air, in order that the lime carbonate may be removed and the phosphate concentrated, though, to a certain extent, this may also occur in the zone of ground water circulation. Next it must be noted that the solution of the lime requires a certain amount of moisture, and thus such deposits are likely to form chiefly during periods of pluvial climate, or those in which rock-salt and gypsum are less likely to form in the same region. Vegetation, characteristic of pluvial climates, may greatly assist in the removal of the limestone by furnishing carbonic acid to the percolating rain water. Hence carbonaceous deposits are not unlikely in association with the phosphates. This is shown by the covering of black bituminous shale, in part of residual origin, in the case of the Tennessee phosphates, and by the presence of graphite in the more metamorphosed phosphates of Wales. In periods of dry climates the limestones may disintegrate, but the material would not be likely to be assorted and the removal by wind or occasional torrents is probable.

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[1] Vaughan, T. W., A contribution to the Geological History of the Floridian Plateau, Carnegie Inst., Publ. 133, p. 182, Washington, 1910.

The residual phosphates must be protected from subsequent removal, either by accumulation in solution hollows as in the case of some of the Tennessee phosphates and in those of Nassau, Germany; or by the formation of a covering stratum of residual soil or material washed in by streams, etc. In the case of the Nassau deposits and those of the south of France as well, the covering deposit is a young alluvial soil or Tertiary river or flood-plain sediment; in the case of the Tennessee and probably also of the Welch deposits, it is residual soil. The rich deposits of Belgium are residual products in the Cipley chalk, concentrated in hollows, and are covered by Tertiary beds. A similar condition obtains in the case of the important deposits of Tunis and Algeria in North Africa, and to a certain extent in the Florida and South Carolina deposits. These are fully described in the stratigraphic chapters. Where the sea has ready access subsequent to the formation of the phosphate concentrate, this is likely to become scattered, forming layers of dissociated nodules, probably at a locality other than that of formation, or these nodules may become secondarily re-embedded in a scattered condition in later marine deposits. This appears to be the case with some of the Cretacic phosphate layers of England.

Phosphate deposits of this type therefore indicate a hiatus in a geological series and represent an unrecorded interval, or a disconformity in the series. Such disconformities can often only be ascertained by the study of the fossil content of the adjoining strata when the absence of an intermediate formation, elsewhere found, is indicated. Deposits of this type may also be looked for at horizons known to represent periods of widespread emergence, by negative eustatic movements of the sea, such being the case with the Welch horizon. This same horizon, known to be widespread in America (between the Galena and Maquoketa formations of the Western United States) may be explored for phosphate deposits with some hope for success, although the fact that the succeeding formation is a marine one, suggests that such deposits are only preserved where they accumulated in solution hollows of the underlying limestone (the Galena).

Terrestrial Deposits of Phosphate of Lime of Organic Origin

These are practically confined to the guano deposits formed by the excrements of birds and bats, and to the bone-beds formed by extensive destruction of terrestrial vertebrates.

Bird Guano.—This is found both as soluble and as insoluble guano. The most important deposits of soluble guano are found on the Pacific Coast of South America, especially on the islands off the coast of Peru. They "consist of the excrements of flamingoes, divers, penguins and other sea fowl, mixed with the carcasses of these birds, as well as those of seals, sea-lions and other marine animals, which inhabit these seas in vast numbers." "The guano is generally pulverulent on the surface, but becomes compact at a depth. It is in some places over a hundred feet in thickness and is white to brown in color."[1] Small lumps containing ammonia salts and others containing large quantities of phosphate of lime or silica often occur, and in some deposits gypsum is abundant.

The phosphates in the guano occur largely as tricalcic, dicalcic, ammonia-magnesic and ammonic phosphates so that a large part of it is in a very soluble form, hence its value as a plant food. There is also in the guano a soluble base called guanine with the formula $C_5H_5N_5O$.[2] For the preservation of these soluble substances, a very dry climate is necessary and this is realized on the Peruvian Coast which lies in the lee of the Andean Chain. This coast too is frequented by enormous flocks of sea birds on account of the vast schools of fish in the waters of this region, which serve as food for the birds.

The richest deposit was found on the small Chincha Islands off the Peruvian coast where the first beds of guano were mined. These islands are rarely more than 3 miles in circumference, and the supply was exhausted by 1872. The material was shipped to England as early as 1842 in which year 182 tons were exported. Many other small islands have been stripped of their deposits.

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[1] Penrose, *loc. cit.*, p. 118.

[2] *Loc. cit.*

The mean of 21 analyses of guano from Macabi Island, Peru gave Barral: Nitrogen, 10.90 per cent.; Phosphates, 27.60 per cent.; Potash, 2 to 3 per cent.[1] (see also Table LXXXIX). Other deposits of guano are found on the Chilean coast, where near Iquique, province of Tarapaca, a mass 10 meters in thickness is known, which is estimated to have been formed in 1,100 years. Near the Cape of Good Hope and northwest of it at Saldanha Bay, other deposits occur. On the southwest coast of Africa similar deposits have been found on the Island of Ichaboe and at Algoa Bay on the southern coast. This is, however, often leached by rain and the sea water, but in part still contains large quantities of soluble salts of ammonia and phosphorus. "The Island of Ichaboe contained 200,000 tons of guano, all of which was removed in fifteen months after its discovery in 1844.

In the following table complete analyses of Peruvian and Ichaboe guanoes are given for comparison.[2]

TABLE LXXXIX.—ANALYSES OF GUANO

	Peruvian	Ichaboe
Water and volatile ammonia	15.27	3.14
Organic matter and ammoniacal salts	51.44	63.52
Chloride and Sulphate of Soda	5.50	5.02
Insoluble siliceous matter	0.57	1.16
Phosphate of Lime and a little Phosphate of Magnesia	21.11	22.20
Carbonates of Lime and Magnesia	6.11	4.96
	100.00	100.00

Soluble guano is also found in Sharks Bay, Australia, on the Kuria Muria Islands, on the coast of Arabia and elsewhere along dry coasts.

Leached Guano.—Guano from which all, or almost all the soluble constituents have been dissolved by rain or the action of sea water is found on many pluvial coasts. It occurs either in pulverulent or in more or less solidified form. It is plentiful on some of the small islands in the Pacific northeast of Australia and especially between latitudes 10° north and south of the equator and between longitudes 150° and 180°W, where there are some 40 guano islands, on a coral reef foundation, and often with a salt water lagoon in the center. Among the islands richest in guano are Baker, Howland, Jarvis, McKean, Malden, Starbruck and Phoenix. Sometimes the soluble portion has been washed into the underlying coral rock phosphatizing it. On Baker Island the following characteristic section is found.

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[1] For other analysis see Penrose, *loc. cit.*, pp. 119–122.

[2] Quoted by Penrose, *loc. cit.*, p. 121.

1. Coral rock containing gypsum.
2. Denser stratum of same substances.
3. Pulverulent yellow leached guano.

In the following table analyses of the several types of phosphate from Baker Island are given.

TABLE XC.—ANALYSES OF GUANO, ETC., FROM BAKER ISLAND, PACIFIC OCEAN (SIGERT)[1]

	1	2	3	4	5
Water	1.45	10.25	9.03	0.90	8.20
Combustible matter (1)	2.57	5.11	4.02	4.47	8.30
Potash	0.10	0.44	0.43	0.46	0.62
Soda	0.45	0.73	0.62	1.21	1.13
Lime	53.78	43.83	43.44	45.82	40.63
Magnesia	0.27	0.42	0.60	1.89	1.75
Phosphoric acid	0.00	33.97	33.62	38.98	37.16
Sulphuric acid	1.40	2.07	6.81	1.16	1.17
Carbonic acid	38.98	3.18	1.43	5.11	1.04
Total	100.00	100.00	100.00	100.00	100.00
(1) Nitrogen	0.00	0.00	0.00	0.00	0.92

1. Unchanged white coral rock.
2. Yellow-brown crust often several inches thick, with white interior of coralline structure.
3. Gray-brown balls, soft to pulverulent often several inches thick, coralline structure fully marked.
4. Porcelain-like cakes, smooth or rough, soft 1 to 4 inches thick, and in parallel plates.
5. Whole guano powdered.

On Jarvis Island the evaporation of the central lagoon has produced a bed of gypsum and over this lies a bed of leached guano from one inch to one foot thick and covered by a phosphatic crust. The bed under the crust contains both basic and neutral phosphate of lime due according to C. U. Shepard, Jr., to the decomposition of the tribasic phosphate by the gypsum. Concretionary nodules composed of interstratified layers of phosphate of lime and gypsum are occasionally found.

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[1] Quoted by Penrose, *loc. cit.*, p. 125.

Many of the coral islands of the West Indies carry leached guano. Among them Sombrero, Navassa, Turk, St. Martin, Aruba, Curacoa, Orchillas, Arenas, Roncadr, Swan, and Guanahani islands are the most important. The Pedro and Morant Keys and the reefs of Los Monges and Aves in Maracaibo Gulf are also important in this respect. There is considerable variation in the deposits of the various localities, in color, form and structure, sometimes it is mammilated at other times it has a concentric structure and it often has a white phosphatic enamel. On Sombrero two types occur: (1) granular porous and friable, of white, pink, green, blue or yellow color; (2) dense, massive and homogeneous, of white or yellow color. It contains 75 to 80 per cent. of phosphate of lime, and many bones, becoming in places a bone breccia. On Navassa Island the phosphate is found in pockets in the living coral and in the numerous depressions and hollows on the island. It is dark brown, of oölitic grain and contains from 10 to 15 per cent. of alumina and iron which is detrimental. On Aruba Island the phosphate is hard and massive and white to dark brown in color. Sometimes the underlying coral rock is phosphatized, containing 70 to 75 per cent. of phosphate of lime.

Leached guano also occurs on islands in the Gulf of California, where on Raza Island, a locality now exhausted, the deposit averaged over 41 per cent. phosphoric acid, corresponding to over 85 per cent. of phosphate of lime.

The annual output from the West Indian islands was from 50,000 to 70,000 tons for Curacoa and 10,000 tons for Sombrero. Many other islands produce much less. The presence in many of the West Indian deposits of large quantities of phosphate of iron and alumina makes them undesirable as sources for superphosphate.

Bat Guano.—This is found in caves, or on cavernous cliffs inhabited by bats. "It consists of the dung of bats mixed with the bodies of their dead, as well as with the remains of rats, mice, etc." These deposits are of limited extent, but are found in many places in America and in the old world. Some of the best known cave deposits in the United States are in Indiana, Kentucky, Alabama, and near San Antonio, Texas; along the Mediterranean coast especially in Italy, many such deposits exist (see also discussion under Nitrate Deposits). For an analysis of bat guano see p. 298.

The more important minerals have been referred to above (p. 288).

Bones of Terrestrial Animals.—It has already been noted in the summary of types of phosphate deposits on a preceding page, that accumulations of the bones of terrestrial animals in caves and about salt-licks form a source of phosphate of lime, for as is well known, that substance forms an important constituent of bones which sometimes carry as much as 58 per cent. tricalcic phosphate. This fact has formerly led many to regard some of the younger phosphate deposits such as those of Southern France, of South Carolina, Florida, etc. as derived by the leaching of such bone beds. While no doubt the bones contributed a certain amount of the phosphoric acid in some of these cases this is probably insufficient to account for the extreme phosphatization of limestones and other rocks thus altered. In the celebrated bone fissures and caverns of France such as those of Quercy, the bones seem to be but little altered and indeed in some cases are themselves enclosed in phosphatized material. The Florida and Carolina deposits are now generally regarded as having derived their phosphoric acid from older marine deposits, by leaching and concentration during periods of exposure. While no doubt phosphates of bone origin exist they are probably not very extensive and no important deposits of undoubted bone-origin are now known.

Secondary Phosphates

With the exception of the unleached guano and of some unaltered bone deposits, probably every extensive accumulation of phosphate of lime is in large measure the result of chemical concentration, resulting in the replacement of limestones and the formation of nodules. Carbonic acid in water acts as a solvent to the organic phosphate of lime and this takes place even on the sea bottom where organic matter is subject to decay. The formation of ammoniacal salts by the decomposition of organic nitrogenous matter furnishes the condition for the redeposition of the phosphate of lime on any nucleus which serves to attract it, as well as in the cavities of foraminiferal and other shells. Thus nodules of phosphate of lime are formed. Similar processes are in operation in the disintegration of limestone or other rocks carrying original scattered particles of organic phosphate. Thus in the weathering of such deposits concentrates consisting of nodules of phosphate of lime are formed. Solution of phosphate of lime is especially active where the original phosphate deposit or concentrate is covered by marshes or swamps in which there is an abundant liberation of CO_2. Where solutions carrying phosphoric acid come in contact with limestone, a reaction will take place, the phosphoric replacing the carbonic acid of limestone. Such phosphatization of limestones is generally very local and is primarily downward resulting in the replacement of the upper part of the limestone in an irregular manner, often penetrating the rock in fissure- or pipe-like manner. This is especially well shown in the phosphatization of the Vicksburg limestone of Florida.

Such circulation of waters carrying phosphoric acid may also result in the formation of vein-like deposits of phosphorite as in the case of some of the Spanish occurrences, more fully described in the section on Palæozoic phosphates (Vol. II).

SUMMARY OF THE OCCURRENCES OF ROCK PHOSPHATES

United States

General Summary.—Before 1914 the United States was producing close to 3,000,000 tons of phosphate rock annually, more than 99 per cent. of which came from Florida, Tennessee and South Carolina, while the rest of the country produced less than one per cent. In 1916 the total output was 1,980,000 short tons valued at $5,897,000.00.

Distribution and Age of the Deposits.—Florida has produced more than 75 per cent., and over 40 per cent. of the product exported before the European war, came from that state. Since the beginning of the war both production and export have decreased. Tennessee comes next as a producer and South Carolina third. The other states rich in phosphate deposits are Kentucky and Arkansas in the southeast, and Montana, Idaho, Utah and Wyoming in the west. The deposits of Tennessee, Kentucky and

Arkansas are of older Palæozoic age and will be more fully described in Chapter XXI, Vol. II. Those of the west are of late Palæozoic (Permic) age, and are discussed in Chapter XXV. In addition to these important Palæozoic phosphate deposits there are others at present of less economic value. Such are the Aluminum phosphate of Mount Holly Springs, Pennsylvania, which are regarded as alteration products, and lie upon Cambric and Ordovicic strata. Phosphate deposits have also been cited from Massachusetts, Virginia and Indiana. The Florida and South Carolina phosphates are of Tertiary age and their discussion is reserved for Chapter XXXVII; Tertiary phosphates are known also from Georgia and North Carolina but they are chiefly of local significance. The percentage of the tricalcium phosphate in the best Georgia deposits, south of Bainbridge, ranges from 72 to 76. In North Carolina phosphates occur in Sampson, Dublin, Pender, Onslow, Columbus and New Hanover Counties all in the southeastern part of the state. Most of these phosphates are prolongations of the South Carolina deposits, but in New Hanover and in Pender Counties a conglomerate or breccia of phosphate occurs in a lime matrix, reaching occasionally a thickness of six feet, but with only 10 to 20 per cent. of tricalcium phosphate.

Alabama too, has Tertiary as well as Cretacic phosphates. In the Ripley formation occur phosphates with 20 to 25 per cent. phosphoric acid, while the Eocenic (Lignitic or Chickasawan) formation contains phosphate nodules with 30 per cent. phosphoric acid.

Production and Available Material.—The following table gives the percentage production of the three leading states from 1912 to 1916.[1]

State	1912	1913	1914	1915	1916
Florida	81.0	82.0	78.0	74.0	76.0
Tennessee	14.2	14.5	18.0	21.0	21.0
South Carolina	4.4	3.5	3.9	4.5	2.7
Other States	0.4	0.2	0.1	0.5	0.3
	100.0	100.0	100.0	100.0	100.0

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[1] R. W. Stone, Our Mineral Supplies. Phosphate Rock, Bull. U.S.G.S., 666-J.

In 1915 the U. S. Geological Survey estimated the total amount of available phosphate rock in the United States as 5,712,000,000 long tons of which 5,367,000,000 long tons occur in the four western states. The remaining 345,000,000 tons are distributed as follows:[1]

Florida	227,000,000 long tons
Tennessee	88,000,000 long tons
South Carolina	9,000,000 long tons
Kentucky	1,000,000 long tons
Arkansas	20,000,000 long tons
	345,000,000 long tons

The total amount of phosphate rock is, however, much less, and cannot be considered inexhaustible.

Other Countries

Canada.—The phosphates of Canada are apatites which occur in the crystalline rocks of Ontario and Quebec. They are more fully discussed in Chapter XIX. Canada produced 937 metric tons of phosphate in 1901, 1,338 in 1905, 1,448 in 1908, 1,341 in 1910 and 563 metric tons in 1911.

Mexico.—Beds of phosphate nodules are found in the Upper Jurassic deposits of the Sierra de Mazapil and Concepcion del Oro. The exact relation of these to the enclosing strata has not been determined, but the probabilities are that they also lie along planes of disconformity (which are not uncommon in these deposits) and that they therefore represent concentration deposits. Their content of phosphoric acid approximates 20 per cent. They appear to be comparable to the Jurassic and Cretacic phosphate nodule deposits of Europe.

South America.—Though phosphate deposits are undoubtedly present in some of the Mesozoic and perhaps younger formations, little is known of their occurrence. The great phosphate deposits of South America are the guano beds of the West coast already described.

Great Britain.—Important deposits of phosphate rock occur in the Ordovicic of Wales and these will be more fully described in Chapter XXI. They cover an area of about 140 square miles with beds 15 to 45 centimeters in thickness, and average 46 per cent. phosphate of lime.

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[1] Phalen, W. C., Phosphate rock in 1915, U. S. Geol. Survey Mineral Resources, 1915, part II, p. 258, 1916.

Phosphate nodules occur in the Lias of Lime Regis in the South of England, these nodules ranging from 6 to 20 cm. in diameter and carrying 60 per cent. or over of $Ca_3 (PO_4)_2$. The green-sands of the Cretaceous (Comanchic and Cretacic) of eastern England are likewise rich in phosphate nodules, as are also certain of the chalk beds. These will be more fully described in Chapter XXVII. Finally there are Tertiary phosphates in Norfolk, Suffolk and Essex but they are less important than those of Cretacic age. Nevertheless a maximum production in 1876 gave 250,000 tons from these Tertiary beds.

The best phosphate deposits of Great Britain are exhausted and those that still occur are of local significance only. In 1901 only 80 tons were produced and in 1909 only 4 tons.

Scandinavia and Finland.—The phosphate deposits of these countries are chiefly apatites in the crystalline rocks, of which the important ones will be more fully noted in Chapter XIX. Phosphatic nodules, etc., are also found in the Cambric and Ordovicic strata of Norway and Sweden but these are, on the whole, of less significance. In 1906 Norway exported 3,482 metric tons of phosphates, but in 1910 and 1911 this had fallen to 703 and 897 metric tons, respectively. Sweden produced 3,895 metric tons in 1902 and 2,929 metric tons in 1904.

Belgium and the North of France.—These important phosphate deposits are primarily concentration products from the weathering of late Cretacic strata, together with secondary enrichments of the underlying beds. They are described at length in Chapter XXVII.

Lower Jurassic (Liassic) phosphates occur in the departments of Yonne, Cote d'Or, Haute-Saône and Cher. These are everywhere in nodules and lie along planes of disconformity or of temporary cessation of deposition of clastic material as more fully discussed under the Jurassic stratigraphy of this region (Chapter XXVII). Belgium produced 202,880 metric tons in 1910 and 196,780 metric tons in 1911. (For France see next section.)

South of France and the Pyrenees.—In the department of Vaucluse and Drôme occur rather unimportant beds of phosphate nodules in the Cretaceous green-sands (Gault). They range from 33 to 58 per cent. tricalcium phosphate.

In the departments of Aveyron, Lot, Tarn, and Tarn-et-

Garonne, the Jurassic strata which there form a series of plateaus, contain fissures and cavities in which deposits of phosphate of lime of younger origin are formed, perhaps as the result of deposition from hot springs. Here belong the famous deposits of Quercy already referred to. They represent a type of secondary phosphate deposit not as yet fully understood, and apparently confined to these Jurassic strata. The percentage of phosphate in these deposits ranges from 50 to 80.

In the Pyrenees, beds of phosphate nodules occur in the departments of Basse Pyrénées, Ariège, Haute Garonne, Aude and Tarn. In parts of Ariège, the nodules form as much as half the mass of the deposit and range from the size of a nut to that of a fist. They belong to the Upper Devonic and are more fully noted in Chapter XXIII. The total production of phosphates in France was as follows: In 1901, 535,676 metric tons; in 1905, 476,720 metric tons; in 1910, 333,506 metric tons and in 1911, 312,204 metric tons.

Spain and Portugal.—Devonic as well as Siluric and older phosphate deposits occur in Spain and these are noted under their respective horizons in the stratigraphic section (Vol. II). Portugal contains phosphate deposits in the Lower Cretaceous (Neocomian) but they are not exploited to any extent. The production of Spanish phosphates in 1910 was 2,840 metric tons and in 1911, 3,520 metric tons.

Italy.—The important phosphates of Italy are of Tertiary age, the Eocenic containing beds of coprolitic and bone phosphates near Gallipoli on the Gulf of Taranto, and the Oligocenic of Sicily and Malta containing phosphatic Globigerina limestones believed to be of deep sea origin. They are more fully noted in Chapter XXXI.

Switzerland.—Rather poor phosphates are found in Eocenic deposits in the canton Schwyz near Einsiedeln. This occursin the Nummulitic limestones. Other localities are Schivytz and Appenzell.

Germany.—The oldest deposits are found in the Siluric of the Vogtland, while the most important German phosphates are those of Nassau in the Rhine district which lie in Devonic limestones and are the product of concentration through weathering. These are more fully noted in the discussion of Devonic phosphates, in Volume II. The best deposits have long since been exhausted the highest production being in 1884 when 54,000 tons valued at 1,469,730 marks were mined. In 1906 only 1,176 tons valued at 15,288 marks, and in 1907, 653 tons valued at 7,383 marks were mined. Cretacic phosphates occur north of the Harz, these being nodules of the type and origin of other Cretacic nodules of Europe. In the Baltic region along the south shore of that water body, phosphate nodules occur in Mesozoic and younger strata, the richest being the amber-bearing greensands of the Oligocenic. Even in the drift of North Germany, phosphate nodules are found, often in significant quantities. The Oligocenic brown-coal bearing formations of Oberfranken also contain phosphate beds from 0.1 to 0.6 meters in thickness but of variable character.

Austro-Hungarian Region.—Lower Cretaceous phosphates of poor quality are found near Kostic and Teplitz and somewhat better ones near Johannisbad in the Schwarzental. These carry 66.79 per cent. $C_3(PO_4)_2$. Other Austrian localities for phosphate nodules are Rakovitz between Kruchowitz and Hindl and Oberlangen and near Starkenbach. Galicia too has phosphate deposits which are the continuation of those of Russia. Hungarian phosphates are obtained at Kobolapajann and Szigola.

Russia.—Phosphate nodules of Siluric age are known from Podolia, southwest Russia. From these Siluric beds the nodules have been separated in later ages and they are now secondarily concentrated in many localities in Cretaceous strata, where they are found along the banks of the Dniester and its tributaries in Podolia and Besserabia. In central Russia phosphate deposits are very wide-spread in the Comanchic and Cretacic deposits and they are more fully noted in the discussion of these horizons (Chapter XXVII). Near Nischni Nowgorod and Moscow phosphate nodules are found in Jurassic strata and near Kynö they occur in Tertiary beds. In 1905 Russia produced 20,586 tons of phosphates but only 13,423 tons in 1909.

North Africa.—Among the most important old world phosphate deposits are those of Algeria and Tunis which lie at the border of the Cretacic and Tertiary formations and represent in part concentration products along a plane of disconformity together with more or less secondary phosphatization. These are described at some length in Chapter XXXI. The Algerian output in 1911 was 738,935 tons and that of Tunis 1,592,000 metric tons. Other deposits occur in the upper Cretacic of Egypt, partly in the Libyan desert region, but more especially between the Nile and the Red Sea and near Mt. Sinai. These too, occupy a plane of disconformity within the upper Cretacic and are in part concentration products. They are described at some length in Chapter XXVII.

South Africa.—The phosphate deposits of Natal consist of phosphatic shales in the Ekka shale series and phosphatic nodules in these shales. The nodules carry as much as 50 per cent. but the shale only about 7 per cent. tricalcium phosphate. Phosphates high in iron and clay are also found near Ladysmith and Brynetown. The export of phosphates from Natal was 349 tons in 1909 and 280 tons in 1910.

Asia.—The Egyptian phosphates are continued into Palestine where they occur in the upper Cretacic of the desert of Judea and the high plateau of the east Jordan district. (See Fig. 72, p. 195.) They continue further into Asia Minor.

Tonkin produces phosphates in the province of Ninh-Binh (27–28 per cent. phosphoric acid) and Japan produces them from Tertiary sandstones and tuffs of the Province of Noto. Tertiary phosphate nodules also occur in Hyuga and older phosphates are found in Palæozoic quartzites of Shima. On the whole, however, the production of phosphates in Japan is a limited one. Guano occurs on some of the islands. In 1909 Japan produced 3,933 metric tons, in 1910, 1,059 and in 1911, 2,268 metric tons.

Australia, New Zealand, Etc.—Australia is not rich in phosphate deposits, so far as known. At Dandaraga occurs a bone bed with 15–39 per cent. P_2O_5, lying upon a somewhat ferruginous sandstone with 7–15 per cent. P_2O_5 and covered by a faintly phosphatic laterite. In 1908 South Australia produced 11,177 metric tons but in 1910 and 1911 the production was only 5,283 and 5,893 tons, respectively. The phosphates of New Zealand occur in Tertiary and Cretacic strata southwest of Dunedin. They contain up to 31.42 per cent. P_2O_5 and reach a thickness of 1.50–2.40 meters.

CHAPTER XV

SALT DEPOSITS OF MINERAL SPRINGS AND FUMAROLES AND OF CIRCULATING GROUND WATER. SALTS OF IGNEOUS ORIGIN

Definition.—The term *mineral spring*[1] is here applied to all springs the water of which carries more than 0.1 permille of salts in solution. The name *hot springs* is here used to cover all waters issuing from the ground, the temperature of which is above that of the atmosphere at the point of exit.

Hot springs are common in regions of active or recently extinct volcanoes, but they are not confined to them, as is shown by the hot springs of Bath, England, with temperatures ranging from 104° to 120°F., and by similar springs of other regions where there is no indication of vulcanism.

The name *geyser* is applied to hot springs the waters of which are ejected periodically and generally with much force (Fig. 101). *Fumarole* is the name applied to jets of steam, impregnanted with vapors of various kinds which issue from the craters of volcanoes and elsewhere in volcanic regions. They also issue from fissures in, and from the surface of cooling lava streams. A part of this steam is, no doubt, derived from the ordinary ground water, but probably a large part is of deep-seated or magmatic origin, being derived from the molten magma. Where the fumaroles deposit native sulphur, they are spoken of as solfataras.[2]

SOURCES AND TYPES OF SPRING WATERS

The water of hot springs may be regarded as surface waters, heated by descent to great depths, or by coming in contact with still hotter igneous masses, or they may be considered as newly formed, juvenile, or magmatic waters. In nonvolcanic regions, surface waters may attain to high temperatures by descending to the requisite depths which can be determined from the known rate of increase in temperature in the earth's crust. Thus Prestwich has determined that the waters of the hot springs of Bath must come from a depth of about 3,500 feet, while Russel estimates that the water of the Mountain Home hot springs of Idaho, which has a temperature ranging from 103° to 167°F. must rise from a depth of 5,000 feet, if the natural increase in temperature is the source of the heat of the spring water.

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[1] In the following discussion, springs carrying mainly calcium carbonate or iron salts are omitted. Deposits of some of these have previously been referred to.

[2] This name is, however, also applied to dying volcanoes in the fumarolic stage.

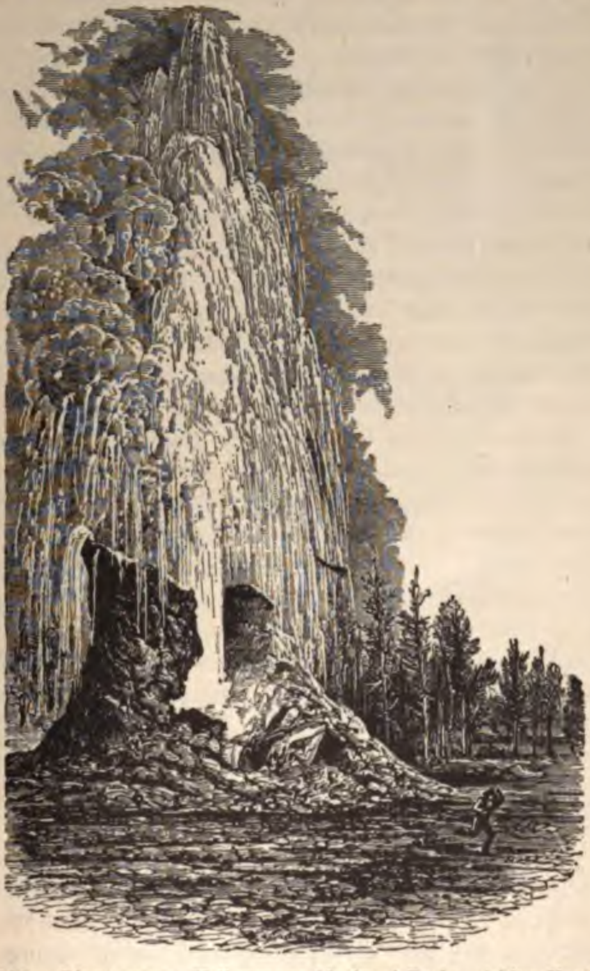

FIG. 101.—Giant geyser, Yellowstone National Park. (*After Hayden.*)

When descending surface waters come in contact with buried hot igneous masses, they may be heated to high temperatures without descending to extreme depths. This is probably the source of all the hot springs in volcanic countries, in so far as they are not of magmatic origin. The 3,000 and more hot springs of the Yellowstone National Park have been regarded as owing their heat to such contact sources, an explanation also applied to the geysers of which there are about 100 in the Park. The view, however, that these hot springs and geysers derive their waters from magmatic sources is held by a not inconsiderable number of students of these phenomena. The magmatic origin of the geyser waters of Iceland is confidently asserted by some.

The term juvenile waters was coined by Professor Edouard Suess for waters derived through the condensation of the emanations of deep-seated igneous magmas. More recently, the term magmatic waters has been applied to them. These waters, while originally hot, may become chilled on ascending through the cooler layers of the crust and issue with a temperature not differing much from that of ordinary spring water. Such appears to be the case with the waters of the Carlsbad Sprudel in Bohemia, which Suess took as the type of his juvenile waters, and with those of the Saratoga Springs of New York, which Kemp and others regard as of magmatic origin.

It is probably impossible in most cases to determine whether the water of a given hot spring is of magmatic or of superficial (Vadose or Phreatic) origin. In some cases there may be a mixture of both in varying proportions, and it is not impossible that two hot springs, one chiefly with magmatic the other mostly with vadose waters may occur in neighboring districts. The composition of the salts carried by the water may serve as an important guide in the determination of this question, but even this may not in all cases be reliable.

In Table XCI, p. 329, are given the analyses of various waters of springs generally held to be either wholly or in part of magmatic origin, though believed by others to be vadose waters. These range from the hot waters of geysers and boiling springs, to the waters of the Carlsbad Sprudel, the type of Suess' juvenile waters. The waters of Borax Lake, Lake County, California, are included as a part of its constituent is derived from hot springs, which are regarded by some as of magmatic origin.

Comments on the Analyses.—The waters of Borax Lake, Lake County, California, situated about 80 miles north of San Fran-

	Borax Lake, Cal	Utah Hot Springs, temp. 55°C.	Koch-brunnen, Wiesbaden, Germany	Boiling Springs, Savu-Savu, Fiji	Congress Spring, Saratoga, N. Y.	Hawthorn Spring, Saratoga, N. Y.	Cleopatra Spring, Yellowstone Park	The Sprudel Carlsbad, Bohemia	Old Faithful Geyser, Yellowstone Park	Grand Geyser, Iceland	Hot Spring, Clear Lake, Cal.
Cl	32.27	58.79	56.58	57.91	42.00	42.42	10.09	11.52	31.64	13.52	16.49
Br	0.04	Trace	0.04	.....	1.13	0.16	Trace	Trace	0.25		
I	.....	.....	Trace	.....	0.02	0.02	.....	Trace	.....	.....	0.03
F	.....	.....	.....	.....	Trace	Trace	.....	0.03			
SO_4	0.13	0.94	0.78	3.38	0.08	.....	30.34	31.19	1.30	9.01	Trace
S	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.32	
CO_3	22.47	0.61	3.13	Trace	18.59	19.28	21.65	19.15	8.78	10.16	21.96
PO_4	0.02	.....	Trace	Trace	Trace	.....	.....	0.01			
AsO_4	.....	.....	Trace	.....	.....	.....	0.26	.....	0.24		
B_4O_7	5.05	.....	.....	.....	Trace	Trace	1.46	.....	1.19	.....	25.61
BO_3	.....	.....	0.01	.....	.....	.....	.....	Trace			
NO_3											
Li	.....	Trace	0.04	.....	0.08	0.16	0.13	Trace	0.40		
Na	38.10	30.38	32.60	16.65	27.62	27.29	7.50	32.49	26.42	19.71	24.99
K	1.52	3.76	1.16	0.93	0.78	0.68	2.95	1.35	1.93	1.88	Trace
RbCs	.....	.....	.....	.....	.....	.....	.....	Trace			
NH_4	.....	.....	0.07	.....	.....	.....	0.03	.....	Trace	0.28	7.88
Ca	0.03	4.90	4.05	18.34	6.03	5.69	17.76	2.23	0.11	.....	Trace
Mg	0.35	0.40	0.61	0.04	3.41	3.92	4.21	0.65	0.04	0.08	Trace
Sr	.....	.....	0.12	.....	Trace	Trace	.....	0.01			
Ba	.....		0.01	.....	0.09	0.12					
SiO_2	0.01	0.20	0.76	1.78	0.14	0.17	2.98	1.34	27.58	45.04	2.64
Al	.....	.....	.....	0.43[1]	.....	.....	.....	Trace			
Al_2O_3		0.02	.....	0.54	Trace	0.02	0.54	.....	0.12	.....	0.40
Fe_2O_3	0.01	.....	0.04[2]	.....	0.03	0.07	.....	0.01[3]	Trace[5]		
Mn_2O_3		.....		.....	.....	.....	.....	0.02[4]	Trace[5]		
As_2O_3											
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille	76.56	23.309	8.241	7.813	12.022	15.238	1.732	5.431	1.388	1.131	5.343[6]

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[1] Reported as $AlCl_3$. [2] Given as Fe″ and Mn. [3] Given as Fe, free CO_2 is also present to the amount of 0.354 ‰.
[4] Given as Mn, free and half combined CO_2 = 0.7604 grams per kilogram. [5] Given as Mn and Fe.
[6] Reckoned with normal carbonates; with bicarbonates the salinity becomes 6.556 ‰.

cisco in the desert region of the great valley, contain chiefly sodium carbonate and sodium chloride, in addition to which there is a considerable amount of borax present. This is deposited in crystals, some of which are several inches long. A neighboring body, Lake Hachinchama, contains an even larger amount of borax. This salt is probably derived from hot springs near the lake (Becker), the analysis of one of which is given in the last column of the table (*K*), and shows a remarkable quantity of boric acid ($B_4O_7 = 25.61$ per cent.), besides an unusually high percentage of ammonia. The salinity of the spring itself is comparatively low, being only 5.343 permille, while that of the lake is much more concentrated, being at the time of analysis 76.56 permille. Utah hot springs, 8 miles north of Ogden, Utah, the Kochbrunnen of Wiesbaden, and the Boiling Spring of Fiji are chloride waters. In the first two, sodium chloride is the dominant salt, with calcium probably as chloride in the first and as carbonate in the second. The Fiji Spring has similar amounts of calcium and sodium, both probably in the form of chloride, though sulphates also are present. The two Saratoga springs are sulphate-chloride waters, with sodium as the principal base, but also with considerable quantities of calcium and magnesium.

Cleopatra springs in the Yellowstone is a triple water with sulphates, chlorides and carbonates all present in considerable amounts. The principal base is calcium, with sodium and magnesium next in abundance. The presence of nearly 3 per cent. of silica is to be expected in an alkaline water. The deposits around this spring, as around the majority of the hot springs of the Yellowstone, are chiefly calcareous sinter, which is in large part, no doubt, precipitated by the breaking up of the bicarbonate and the escape of the extra molecule of CO_2 on cooling. A considerable portion of the lime of these springs appears to be precipitated, however, by the aid of lime-secreting algæ. These lowly plants have been found to occur in the waters of the hot springs of the Yellowstone, where the temperature ranges between 90° and 185°F., a larger number occurring in the warmer water. These plants abstract the extra molecule of the bicarbonate and thus cause the precipitation of the simple carbonate. The reaction here is the same as in the case of purely inorganic precipitation, namely $CaH_2C_2O_6 = CaCO_3 + H_2O + CO_2$. An analysis of the sinter of the Mammoth Hot Springs of the Yellowstone gave CaO 52.46, and CO_2 40.88, with minor amounts of MgO,

K_2O, Na_2O, NaCl, silica, alumina, iron, and organic matter (see *ante*, Table XLI, p. 207).

The Carlsbad Sprudel of Bohemia has long been famous not only for its reputed therapeutic properties but for the deposits which are formed by these springs. The water, as shown by the analysis (*H*), is a triple water with sulphates, carbonates and chlorides all well represented. The principal base is sodium, calcium being present only in moderate amount. Nevertheless the deposits are chiefly of carbonate of lime. The most remarkable of these deposits are the Carlsbad pisolites. These are spherules of $CaCO_3$ incrusting minute particles of quartz or feldspar which were held in suspension by the rising waters and were turned in all directions so that the incrustations became uniform all around. Sometimes gas and air bubbles form the nuclei of these incrustations, the center of the sphere thus being hollow. The composition is $CaCO_3$ with usually a small quantity of $FeCO_3$. The mineral is neither calcite nor aragonite, but a third modification known as "Ktypeit," which by heat is convertible into calcite.[1]

Calcareous sinter is deposited from the Sprudel waters by the aid of lime-secreting algæ. The lime is deposited first in minute crystals in the slime between the vegetable threads (Oscillariæ) and upon their surface. At first these crystals are separate but continue to grow in numbers, producing star-like clusters which by enlargements grow into grains of calcareous sand. By further growth these grains unite into a solid mass of travertine.[2]

The geyser waters given in the table show comparatively low salinity. The water of Old Faithful is a chloride-carbonate water with sodium as the principal base; that of the Icelandic geyser a triple water with sodium as the principal base. Calcium and magnesium are absent or present in small quantities only. This makes the waters essentially alkaline and this added to their high temperature favored the solution of silica, which is present in large quantities in both waters. This silica is deposited around the mouth of the geyser in the form of siliceous sinter or geyserite. Mineralogically this is a species of opal, for it consists mainly of hydrated silica with impurities in variable amounts. In the following table analyses of the sinter deposited by Old Faithful and other geysers are given.[1]

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[1] Zirkel, F. von, Lehrbuch der Petrographie, Band I, p. 488, 1893; Hochstetter, F. V., Karlsbad, seine geognostische, Verhältnisse und seine Quellen Karlsbad, 1856.

[2] Ferdinand Cohn, 1862, Die Algen des Karlsbader Sprudels mit Rücksichs auf die Bildung des Sprudel Sinters, Abhandl. d. Schlesischen Gesell. d. Naturwissensch. Heft 2, pp. 35, *et. seq.*

TABLE XCII.—ANALYSES OF SILICEOUS SINTER FROM GEYSERS

	A	*B*	*C*	*D*	*E*
	Old Faithful geyser, compact sinter	Excelsior geyser basin, Yellowstone incrustation	Giant group upper basin, Yellowstone geyserite	Geyserite from Iceland	Geysers of Rotorua, New Zealand, sinter
SiO_2	89.54	94.40	72.25	87.67	92.47
Al_2O_3	2.12	0.79	10.96	0.71	2.54
Fe_2O_3	Trace		0.76		
FeO	.....	......	0.31		
CaO	1.71	......	0.74	0.40	0.79
MgO	Trace	......	0.10	......	0.15
K_2O	0.30	......	1.66	Trace	
Na_2O	1.12	......	3.55	0.82	
NaCl	Trace	......	0.36		
H_2O (ignition)	5.13	5.02	9.02	10.40	3.99
C	.....	......	0.20		
SO_3	Trace	......	0.45		
	99.92	100.21	100.36	100.00	99.94

Of this series the sinter incrustations of the Excelsior geyser basin are the purest, consisting of hydrated silica with a very small admixture of iron and alumina. The geyserite of the Giant group is the most impure, containing large quantities of Al_2O_3 and considerable proportions of the oxides of the alkalies. The Icelandic and New Zealand geyserites and sinters are also relatively pure.

The distinction between geyserite and siliceous sinter is not always very marked. Geyserite is usually very porous and often fibrous. It contains from 9 to 13 per cent. of water.[2] Siliceous sinter is more compact and contains a smaller percentage of water.

According to W. H. Weed,[3] who investigated the silica deposits of the Yellowstone Park, the precipitation of silica is brought about in a number of ways. Cooling and relief of pressure are among the most effective, and chemical reactions and vaporation are other means. Besides these, algæ living in the hot waters bring about such precipitation of silica, which is at first deposited in and upon the plants in the form of a gelatinous substance, often quite brilliantly colored, being golden-yellow, orange, red, and in the hottest waters, pale flesh-pink or even white. The algæ are often so thickly incrusted by silica that the plant structure is not recognizable even under the microscope, when their presence can only be inferred from the color of the deposit. The color varies with the temperature, even within the same pool, the range with progressive cooling being white, pale flesh pink, bright orange, yellowish-green and emerald. The method by which the algal effect the separation is not fully understood, but it appears to be due to the physiological activities of the plant, for both the algæ filaments and their slimy envelope are formed of gelatinous silica. On the death of the algæ, a loss of a large part of the water occurs and the silica changes to a soft cheesy, but more permanent form. On remaining in the cold water of the pools, there is a further separation of silica, possibly due to reaction of organic acids formed by the decaying vegetation upon the silica salts of the water. This newly separated silica hardens the existing structures in certain cases and covers them with a frost-like coating of silica. (Weed, *loc. cit.*, p. 664.) Similar conditions have been found to exist in the New Zealand hot springs. Certain genera of algæ (*Calothrix, Mastigonema*) form furry sinters and others (*Leptothrix*) produce fibrous or straw-like masses. Diatoms are also very active, especially in the tepid waters, forming beds of diatomaceous earth, and mosses (*Hypnum*) likewise aid in the separation of the silica.

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[1] From Clarke, pp. 206, 207.

[2] Iddings "Rock Minerals," p. 543.

[3] U. S. Geol. Surv., 9th Ann. Rept., 1889, pp. 613–676 (657); also Amer. Jour. Sci., 3d ser., Vol. 37, 1889, p. 351.

Besides the silica, a considerable variety of other deposits are formed from the waters of geysers and hot springs of the silica-depositing type, most of which are, however, high in silica (up to 50 per cent. or over). Some are high in Fe_2O_3, others contain an abundance of MnO and Mn_2O_3 while still others contain a high percentage of the carbonates and sulphates of the alkalies, especially of sodium. Deposits formed by the Constant and Arsenic geysers contain a large percentage of As_2O_3, which separates in the form of the mineral scorodite ($FeAsO_4.2H_2O$), and native sulphur is deposited by some of the waters from hot springs.

Besides these, calcium carbonate is not an infrequent constituent of the deposit.

WATERS OF VOLCANIC ORIGIN

That waters can be condensed from the emanations of molten magmas as well as from superheated igneous rocks has been abundantly shown by experiments. The most elaborate of these were made by Day and Shepherd in 1912, on the lavas of Kilauea under conditions which precluded contamination by surface waters. They succeeded in condensing 300 cubic centimeters of water from the lava in about 15 minutes, and this water, preserved in sealed tubes, as well as the attendant gases, was subsequently analyzed.[1]

The gases consisted of CO_2, CO, H_2, N_2, and SO_2, no chlorine or argon being found, proving that they were uncontaminated by atmospheric air.

The analyses of the waters condensed from these lavas gave the following results.

TABLE XCIII.—ANALYSES OF WATERS CONDENSED FROM THE LAVAS OF KILAUEA (DAY AND SHEPHERD)

	Tube 1, grams	Tube 2, grams	
Na_2O	0.0214	0.031	The major portion of these may have come from the glass containers or from Pele's hair.
K_2O	0.0102	0.011	
CaO	0.0120	0.140	
Fe_2O_3 Al_2O_3	0.0800	0.010	
Cl	0.2200	0.206	
F	0.5650	0.492	
NH_3	0.0018	None	
TiO_2	0.0050?	None	
Total S as SO_3	0.4800	0.508	
Total	1.3954	1.398	

In the table on the following page the composition of several waters from volcanic sources are reproduced from those brought together by Clarke.

Comments on the Analyses.—All these waters except that of Steamboat Springs, contain free hydrochloric or sulphuric acids or both. In the waters of Steamboat Springs, sodium chloride

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[1] Bull. Geol. Soc. Amer., Vol. 24, 1913, p. 573.

TABLE XCIV.—ANALYSES OF VOLCANIC WATERS FROM VARIOUS SOURCES

	A	B	C	D	E	F	G	H	I	J	K
	Steamboat Springs, Nev.	Devil's Inkpot, Yellowstone	Acid Springs, Cal., geysers, Sonoma Co., Cal., Temp., 60°C.	Rio Vinagre, Colombia	Solfatara Possuoli, Italy	Brook from crater of Idjen volcano, Java	Hot Lake, White Island, Bay of Plenty, N. Z.	Cameron's Bath, Rotorua geyser district, N. Z.	Yellow Lake, crater of Taal volcano, Luzon, P. I.	Green Lake, crater of Taal volcano, P. I.	Mother liquor, Tuscan Lagoon water
HCl free	.....	0.18	.....	35.92	.....	43.96	65.42	5.60	.....	13.04	
H_2SO_4 free	.....	1.29	49.71	1.89	16.62	.....	.....	59.11	5.87	2.48	
H_3BO_3	.....	2.73	.....	.....	.....	.....	.....	.....	.....	.....	26.92
Cl	35.00	.....	.....	4.75	0.34	14.95	11.69	.....	47.26	44.52	0.39
SO_4	4.58	67.66	33.92	43.97	55.08	26.96	10.64	20.21	9.50	6.40	49.37
S	0.22										
CO_3	5.08										
PO_4	0.03	.....	.....	.....	.....	.....	1.91	Trace	1.26	0.73	
B_4O_7	8.88	.....	.....	.....	.....	.....	Trace	.....		.	
BO_2 in borates	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	2.50
Na	30.35	0.73	0.58	3.08	Trace	1.32	0.75	8.35	24.14	20.75	0.89
K	3.79	0.24	0.10	.....	0.57	0.39	0.59	0.32	1.38	3.03	1.01
Li	0.27	0.01									
NH_4	.....	22.85	.....	.....	0.58	.....	.....	.....	.....	.....	16.71
Ca	0.25	1.18	0.41	2.45	2.91	2.05	2.30	0.47	0.56	0.22	0.16
Mg	0.01	0.36	5.72	.....	0.55	0.94	0.34	0.22	0.98	1.02	1.99
Mn	.....	.....	.....	.....	Trace	.....	Trace	.....	.....	.....	Trace[1]
Fe''	Trace	Trace	1.92	.....	3.47	.....	.....	.....	0.78	1.03	
Fe'''	.....	.....	.....	.....	.....	4.06	5.98	0.33	5.35	5.55	
Al	.....	0.10	1.02	7.14	7.16	4.44	0.35	Trace	0.55		0.06[2]
Al_2O_3	0.01										
As	0.10	.....	.....	.....	Trace						
Sb	0.02										
Hg	Trace										
SiO_2	11.41	2.67	6.62	0.80	12.72	0.33	0.03	5.39	2.37	1.23	Trace
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Salinity in permille	2.850	.....	.....	.....	.....	.....	.....	.....	.....	.....	18.548
Total impurities, parts per thousand including free acids	.....	3.365	5.467	2.969	2.477	18.060	158.051	1.862	26.989	60.023	

[1] Given as Mn_3O_4.

[2] Part of Al replaced by Fe.

is the chief salt, but sulphates, carbonates, and borates of the alkalies also occur. Carbonates are absent from the other waters, but borates occur in some of them.

The waters of the Devil's Inkpot in the Yellowstone Park (*B*) are of slight acidity and in addition contain free CO_2, amounting to 65 parts, and H_2S amounting to 5 parts per million. The most remarkable feature of the salinity is the high percentage of NH_4, amounting to about 83 per cent. of the total impurity. It occurs chiefly, if not wholly, as ammonium sulphate. As such it would amount to 2.8 grams per liter. The presence of borates in association with ammonium is further noteworthy. Acid Spring, California Geysers, in Sonoma County, California, is a solution of sulphate only, with a large proportion of free sulphuric acid, though the actual salinity is comparatively low.

The waters of the Rio Vinagre, Colombia, fed from volcanic sources, contain both sulphates and chlorides, the former predominating. They contain moreover a large percentage of free HCl and some free H_2SO_4. Boussingault[1] has estimated that the Rio Vinagre at Purace carries each day 46,873 kilograms of H_2SO_4 and 42,150 kilograms of HCl. This, according to Clarke, amounts, respectively, to 17,000 and 15,000 metric tons per annum.

The water from the Solfatara of Pozzuoli is a sulphate solution with free H_2SO_4 and a small quantity of chlorides, while that of the Javanese volcano is a sulphate chloride water with a large amount of free HCl. The Hot Lake of White Island, New Zealand (*G*) is practically a 10 per cent. solution of HCl with some chlorides, sulphates, and a smaller amount of phosphates. Cameron's bath carries sulphates in solution, together with a large amount of free H_2SO_4 and some free HCl. The crater lakes of Taal in the Philippines are strong solutions of chlorides and sulphates, with free H_2SO_4, and in the Green Lake also free HCl. The acids of volcanic waters are, according to J. B. Boussingault,[2] the products of decomposition within the crater. Thus HCl may be generated by the action of steam upon a mixture of chlorides and silica, while hot gaseous HCl will liberate sulphuric acid from sulphates. By the turning of sulphur to SO_2 by volcanic heat, and by the oxidation of this in the presence of moisture, H_2SO_4 is produced. This, in aqueous solution, decomposes chlorides and liberates HCl. Thus there is a complete cycle of decomposition and the acidity of any volcanic water is due to local causes. As an illustration of this may be taken the analyses of the two crater lakes of Taal volcano in the Philippine Islands, which show striking differences in acidity.

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[1] Annals Chem. Phys., 5th ser., Vol. 2, 1874, p. 81.

[2] Ibid., p. 76.

DEPOSITS FORMED FROM VOLCANIC WATERS

The Borax Lagoons of the Tuscan Fumaroles.—In the Italian compartimento of Tuscany are located the famous borax-depositing fumaroles or saffioni. These are jets of steam carrying boric acid which emerge from the ground and supply a large quantity of that substance for commercial purposes.[1] Ammonium salts accompany the boric acid deposits of these fumaroles. (Fig. 102.)

By the condensation of the steam of the fumaroles, lagoons are formed which have a content of solid matter ranging from less than 1 to more than 7 grams per liter. Boric acid (H_3BO_3) is the chief constituent of these lagoon waters, amounting in the condensed waters of the lower lagoon of Monte Rotondo to 19.3 grams per liter. Ammonium sulphate accompanies the boric acid, as the chief salt in solution, the other constituents being small. The precipitate in the lagoons is mixed with clay and colored a dark brown by iron sulphide. In it C. Schmidt has recognized gypsum, ammonium sulphate, ammonium thiosulphate, ammonium sulphide, ammonium carbonate, magnesia, and a little soda and potash. The boron compounds deposited in the lagoons include the following mineral species (Clarke, p. 243).

Sassolite	H_3BO_3 (orthoboric acid)
Larderellite	$(NH_4)_2B_8O_{13}.4H_2O$
Bechilite	$CaB_4O_7.4H_2O$ (borocalcite)
Lagonite	$Fe'''_2B_6O_{12}.3H_2O$

The analyses of the mother liquor of the lagoons after most of the boric acid had been deposited, is given in the last column of Table XCIV (*K*) reduced to standard form by Clarke from figures given by C. Schmidt.[2]

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[1] C. Schmidt, Ann. Chem. Pharm., Vol. 98, 1856, p. 273, Vol. 102, 1857, p. 190.

[2] *Loc. cit.* For methods of extraction see A. Payren, Acid borique des suffioni de la Toscani, Annales de Chimie et de Physique, 3d ser., Vol. 1, 1841, pp. 247–255.

H. Schiff, Ber. Deutsch. Chem. Gesell., Vol. 11, 1878, p. 1690.

Other Deposits of Volcanic Origin.—In the Puga Valley, Province of Rupchu in Cashmere, North India, extensive borax deposits are found, covering the ground to an average depth of

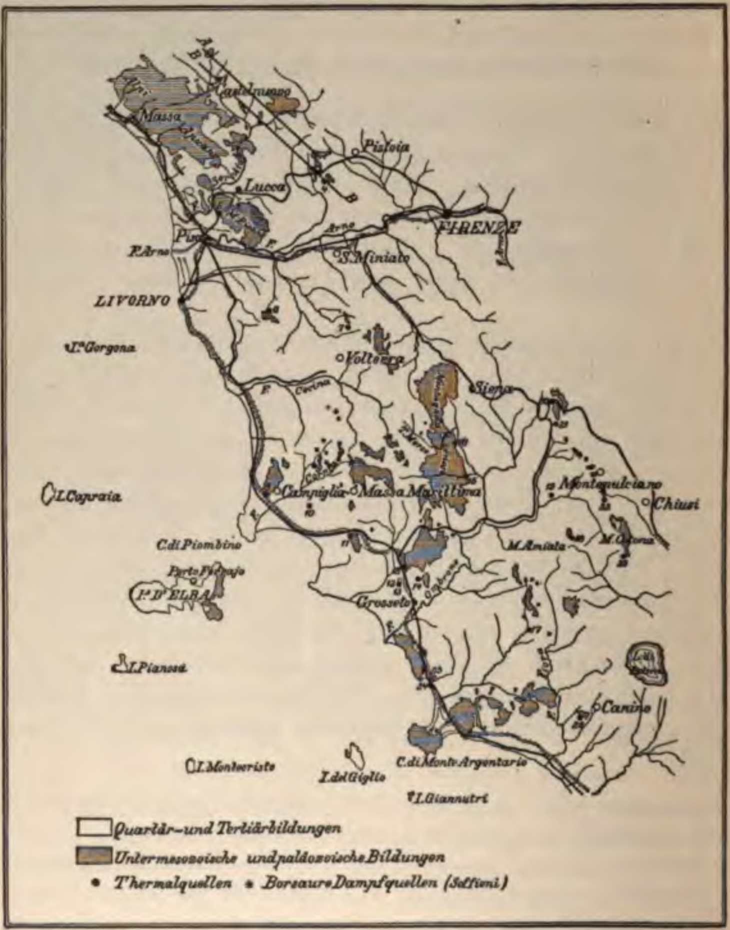

FIG. 102.—Geological sketch map of part of Tuscany, showing the location of hot springs (solid dots .) and Borax Fumaroles or Saffioni (asterisks *). The shaded areas indicate lower Mesozoic and Palæozoic, the white Tertiary and Quaternary formations. Scale approximately 1:200,000. (*Zeitschr fur Prakt. Geologie*, 1893, p. 373.)

three feet. The borax is derived from hot springs which issue at an elevation of more than 15,000 feet above sea level and have a temperature ranging from 54° to 58°C., while the stronger ones have a temperature of 72.5°C. The air temperature at this elevation is 1.3°C. for the yearly average. The deposit also includes free boric acid, sulphur, sodium chloride, ammonium chloride, magnesium sulphate, and alum. Much gypsum also occurs in the vicinity[1] as beds of cement of recent conglomerates.

The Puga is a branch of the Indus, and the region is underlain by crystalline schists (metamorphic), while in the neighborhood are diorites and greenstones. No volcanic or basaltic rocks occur. The length of the basin in which the borax springs occur is a little over 4 English miles, its width from 1,420 to 1,480 feet where the thermal springs reach the surface. Low cones of borax are often built up, some of which rise from 15 to 20 feet above the surrounding borax plain. The stream flows through the deposit of the borax which has a length of something over 10,000 feet and fills the valley for a width of over 1,400 feet. The borax deposit is modified by the admixture of sulphur and boric acid, both of which are often abundant. The surface of the deposit is rough and somewhat weathered, and often covered by wind-borne sand or dust.

The mud volcanoes (Sulsen) of the peninsula of Kertch near the sea of Azov, also deposit borax and other substances.[2] Borax is generally found in the extruded mud of the craters, forming an efflorescence on the dried mud streams, and also occurring in solution in the waters of the pools and marshes. The temperature of these mud flows is a very low one. Besides the borax, the efflorescence on the dried mud flow contains sodium carbonate and chloride, borax, however, predominating. As older analyses of these muds mention no boron, it is possible that a recent change in the source of the material erupted has occurred here. The possibility, however, that the older analyses are of muds leached of their borax by rain water must not be overlooked.

The Colemanite deposits of the Tertiary beds of southern California (12 miles north of Daggett and in the Funeral Mountains) mentioned in a previous chapter, p. 269, have been regarded by Campbell as probably of volcanic origin, this explanation being strengthened by the occurrence of volcanics in the deposits which enclose the Colemanite. H. S. Gale, however, regards these deposits as vein minerals.[1] D. Forbes observed calcium borate, either ulexite or bechilite, actually in process of deposition at the hot springs of Bonos del Toro in the Cordilleras of Coquimbo,[2] and he attributes the borates of the nitrate deposits of Chile to fumarolic sources.[3] Borates also occur in the salares of Argentine (Los Andes, Jujuy, Salta, and Catamarca), the source of the boric acid being ascribed to geysers and hot springs that followed the intense volcanic activity to which the region had been subjected.[4]

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[1] H. von Schlagintweit Sakünlünski, "Ueber das Auftreten von Bor Verbindungen in Tibet." Sitzungsberichte Akademie der Wissenschaften zu München (Mathematish Physikalische Classe), Vol. 8, 1878, pp. 505 538.

[2] W. S. Vernadsky and S. P. Popoff, Zeitschr. für Prakt. Geol. Bd X, 1902, p. 79. (Uber den Boraxgehalt von Eruptionsproducten aus dem Salsengebiet von Kertsch and Taman.)

GASES FROM LAVAS AND FUMAROLES

The gases which are condensed from fresh lavas and which issue from fumaroles, comprise besides the water vapor, chiefly free CO_2, nitrogen or SO_2, with other substances in lesser quan-

TABLE XCV.—ANALYSES OF VOLCANIC GASES

	Gases from lavas of Kilauea, Day and Shepherd					6 Fumarole, Great Crater of Hecla, Iceland, Bunsen	7	8	9	10 Mont Pelée temp. about 400°, Lacroix
							Crater of Volcano, fumaroles			
	1	2	3	4	5		Temp. above melting point of lead, Deville and Le Blanc	Temp. above 350°, Fouqué	Temp. 150°, Fouqué	
CO_2	23.8	58.0	62.3	59.2	73.9	2.44	None	23.40	50.62	15.38
CO	5.6	3.9	3.5	4.6	4.0	......	....	......	.....	1.60
CH_4	.....	....	....	.....	.....	......	....	......	.....	5.46
H_2	7.2	6.7	7.5	7.0	10.2	......	....	......	.....	8.12
O_2	.....	....	....	.....	.....	14.21	10.10	0.52	2.20	13.67
N_2	63.3	29.8	13.8	29.2	11.8	81.81	50.77	2.28	10.99	54.94
A	.....	....	....	.....	.....	......	....	......	.....	0.71
SO_2	None	1.5	12.8	None	None	1.54	39.13	73.80	27.19	Trace
HCl	.....	....	....	.....	.....	......	....			
S vapor	.....	....	....	.....	.....	......	....	......	.....	Trace
	99.9	99.9	99.9	100.0	99.9	100.00	100.00	100.00	100.00	99.88

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[1] H. S. Gale, The Origin of the Colemanite Deposits, Prof. Paper, U. S. Geol. Surv. No. 85, 1913, pp. 3–9 (see also p. 274 *ante*).

[2] Philos. Mag., 4th ser., Vol. 25, p. 113, 1863.

[3] Quart. Journ. Geol. Soc., London, Vol. 17, 1861, p. 7.

[4] Miller and Singewald, The Mineral Deposits of South America, 1919, pp. 52–53.

tities. That these gases of the lavas in the crater and those of the fumaroles do not include atmospheric air is shown by the absence of argon, though a small amount of this has been found in the gases of Mont Pelée, and other West Indian fumaroles, as well as in those of Vesuvius. Atmospheric air also seems to be present in the gases arising from surface lavas. In the preceding table are given, first, five analyses of the gases, obtained from the lavas of Kilauea by Day and Shepherd, followed by 5 analyses of gases from fumaroles. In general, there is a decided change in the composition with change in temperature, as is especially shown by the changes in the fumaroles as we proceed away from the volcanic center, or in the progressive cooling of the lava.

DEPOSITS FROM VOLCANIC GASES

Many deposits of salts are formed direct as sublimates from volcanic or fumarolic gases and emanations, while others are the result of reactions between these gases and salts previously deposited or between them and the igneous rocks of the volcanic region.

Around the fumaroles of Hecla, the analyses of the gases of many of which varied greatly from the one given, Bunsen found deposits of sulphur and various chlorides, especially NaCl. One sublimate contained 81.68 per cent. of ammonium chloride. The fumarole in the crater of Volcano examined by Deville and Leblanc (Analysis 7) deposits boric acid. Around the roots of the other fumaroles (Analyses 8 and 9), realgar, ferric chloride and ammonium chloride were deposited. Other sublimates and products resulting from the action of the gases on the volcanic rocks, which are formed by the fumaroles of Volcano, are, according to A. Bergeat,[1] boric acid, sodium chloride, glauberite, lithium sulphate, sodium sulphate, potash alum, hieratite (K_2SiF_6), and compounds of cobalt, zinc, tin, bismuth, lead, copper and phosphorus. The fumarole of Mont Pelée deposits ammonium chloride and sulphur, and sulphates of sodium, potassium, calcium, magnesium, and aluminum were also found by Lacroix among the fumarole products of this volcano.[2]

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[1] Die Aeolischen Inseln., Abhandl. Math. phys. Classe K., Bayer. Akad. Vol. 20, Abth. 1, 1899, p. 193.

[2] Compt. Rend., Vol. 144, 1907, p. 1397; Bull. Soc. Minn., Vol. 28, 1905, p. 60.

The fact that many of the substances deposited around the mouths of fumaroles are not found in the analyses of the gases indicates that such deposition takes place at the escapement of the gas. Many of the products found are the result of the action of the heated gases on the lavas. On the chemistry of these reactions an extensive literature exists, with which we are not here concerned.[1] From our point of view the important fact is that many soluble salts are formed around the vents of volcanoes and their fumaroles and that these may by solution and secondary concentration form deposits of salts of considerable extent and importance.

The more common of such salts may be tabulated as follows:

Chlorides:

$NaCl$, NH_4Cl, KCl, $CaCl_2$,$MgCl_2$, ferric and ferrous, and other metallic chlorides. Mixed chlorides of Na and K also occur.

Sulphates:

Na_2SO_4, K_2SO_4, $CaSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, Li_2SO_4, Glauberite ($CaSO_4$.-Na_2SO_4).

Carbonates:

Na_2CO_3 (secondary).

Borates and Boric Acid:

Boric acid, Ulexite, Bechilite.

Though chlorine is generally absent from the gases examined, the fumaroles of Volcano were found to contain an abundance of HCl, this being most frequent in the hottest gases, as shown by Analyses 8 and 9 of the table. The surface of fresh lavas of Etna, acting like one great fumarole, emits white fumes which are partly condensed into a saline residue and a small amount of liquid holding free HCl and sulphuric acid. Such residues are

TABLE XCVI.—SALINE RESIDUES FROM SURFACE OF LAVA OF ETNA

	1	2	3
$NaCl$	50.19	63.02	76.01
KCl	0.50	0.27	0.03
Na_2CO_3	11.12	6.49	2.11
Na_2SO_4	1.13	Trace	0.75
H_2O	30.76	30.22	21.10
	100.00	100.00	100.00

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[1] For a condensed summary see Clarke, "Data of Geochemistry," pp. 269–274.

formed on the surface of the lava, their composition being shown in Table XCVI, on the preceding page.

The derivability of both sodium chloride and carbonate, as well as sodium sulphate and KCl from volcanic sources is thus clearly shown. According to the researches of O. Silvestri,[1] both acid and alkaline fumaroles are formed upon the cooling lava streams, the latter at the lower temperature. The acid fumaroles emit much hydrochloric acid and also contain ferric chloride, while the alkaline fumaroles are free from these and deposit only ammonium chloride. In these gaseous exhalations from surface streams much air seems to be present, the nitrogen content ranging from 81.19 to 84.17 per cent. With further cooling, water fumaroles are formed which give off only water vapor mixed with impoverished air. This occurs at relatively low temperatures. Finally, the last phase of activity is marked by fumaroles emitting water vapor and carbon dioxide.

Investigations on Cotapaxi[2] have also shown that hydrochloric acid is abundant in the fumes near the crater, there being even a suspicion of free chlorine. At lower levels hydrogen sulphide and occasionally sulphur dioxide were noted.

NON-METALLIC SALTS, OTHER THAN SILICATES, OF IGNEOUS ORIGIN

The salts formed by the crystallization of igneous magmas are in the main silicates, which as more or less definitely and intimately commingled or interlocked crystals, constitute the main mass of the igneous body. Segregation of certain salts, especially metallic oxides and native metals, may occur during the process of crystallization, resulting in the formation of contemporaneous or syngenetic igneous ore bodies. Non-metallic salts, too, are occasionally segregated in this manner, the silicates, of course, predominating. There are, however, at times non-silicates which appear to be formed in this manner, and of these the more common ones include the following:

Oxides

Quartz (SiO_2).—This occurs most frequently as primary segregations of considerable size only in pegmatites. The form known as tridymite occurs frequently in volcanic lavas, especially the more siliceous and feldspathic kinds.

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[1] O. Silvestri, Neues Jahrb., 1870, pp. 51, 257, abstract by G. Von Rath.

[2] T. Wolf, Neues Jahrbuch, 1878, p. 163.

Corundum (Al_2O_3).—This occurs as the pure crystallized gem form ruby and sapphire, as ordinary crystals, as black corundum, as sand corundum, and as emery, an intimate mixture with magnetite or hematite. Corundum is found in igneous and metamorphic rocks and in alluvial deposits. In igneous rocks (peridotites, pyroxenites, amphibolites, anorthosites, kyshtymites, gabbros, norites, plumasites, diorites, basalts, tonalites, andesites, trachytes, monchiquites, granites, syenites, nepheline syenites, quartz porphyry and pegmatites). It is either a direct constituent of the more acid intrusives or it occurs as segregated masses near the periphery of the basic intrusive masses or is associated with inclusions that have been picked up by the intrusive rocks. In the metamorphic rocks (serpentine, gneiss, mica-schist, quartz-schist, amphibolite schist, chlorite-schist, crystalline limestone, corundum schist, graphite, etc.) the corundum is either one of the original constituents of the metamorphosed igneous rock or is the result of regional metamorphism by which shales, bauxites, or other aluminous minerals have been converted into corundum, or it may be due to contact metamorphism, the corundum occurring in the narrow zone adjoining the intrusive body. In alluvial deposits the corundum is the product of erosion of other corundum-bearing rocks.

Corundum in Commercial Quantities.—Throughout the Appalachian region from Alabama to the Gaspé Peninsula, a distance of more than 1,600 miles, corundum occurs at intervals in peridotites, especially dunite or other basic magnesian rocks, which cut the ancient crystalline belt of eastern North America. The corundum is concentrated either near the contact of the peridotite and the gneissic rocks or in pockets within the mass of the peridotite. In "border veins" between the dunite and gneiss, there is often a sequence of rock and mineral masses, such as is illustrated in the following ideal cross-section of the deposit at Corundum Hill Mine, North Carolina (Fig. 103). The "interior veins" or masses within the dunite also show a banded appearance, as shown in Fig. 104 from the same region. In some of these localities the igneous rock with which the corundum is associated is pyroxenite, amphibolite, anorthosite, and near Peekskill in Westchester County, norites of the Cortland series.

Pratt holds that the peridotite magma holding in solution the chemical elements of the different minerals acts like a saturated liquid from which, on cooling, the minerals crystallize out, not according to their fusibility but according to their solubility in the molten magma. Hence the more basic oxides containing no silica, the chrome spinel and corundum, would be the first to separate out, these being the most insoluble. In a peridotite intrusive the corundum is concentrated toward the border, making a sharp and nearly regular contact with the gneiss, and a sharp and regular, or an irregular contact with the peridotite with masses of the corundum penetrating into it (Fig. 105).

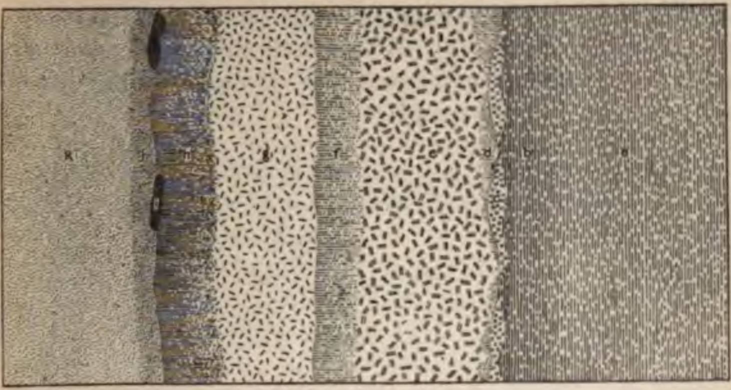

FIG. 103.—Ideal cross-section of a corundum border vein at the corundum Hill mine, North Carolina. *a*, Fresh and unaltered gneiss; *b*, decayed and unaltered gneiss; *c*, vermiculites; *d*, green chlorite; *e*, corundum-bearing zone; *f*, green chlorite; *g*, enstatite; *h*, talcose rock; *i*, clay; *j*, altered dunite; *k*, unaltered dunite. (*After J. H. Pratt.*)

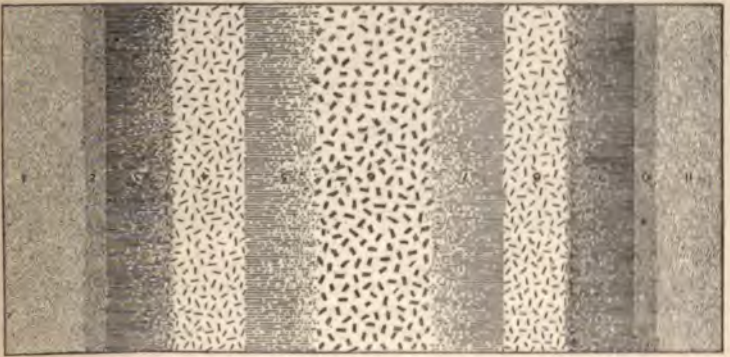

FIG. 104.—Cross-section of an interior vein at a shaft near southern parts of Corundum Hill, North Carolina. 1. and 11. Dunite, hard and apparently unaltered. 2 and 10. Dunite, somewhat friable and discolored, passing into 3. 3 and 9. Talcose rock, fibrous, passing into 4. 4 and 8. Enstatite grayish and somewhat fibrous. 5 and 7. Green chlorite, 6 to 15 inches in width. 6. Green chlorite, corundum and spinel, 6 to 8 feet wide. (*After J. H. Pratt.*)

Corundum, often in gem form, occurs more or less sparingly in cryptocrystalline igneous rocks such as trachytes, andesites, and basalts, in the Auvergne volcanic district of France, and in Germany and North America. It has been found in grains or small masses and crystals in granites, syenites, generally sparingly but sometimes constituting up to over half the rock mass. Pegmatites more rarely carry corundum, though in a few cases it has been found in some quantity.

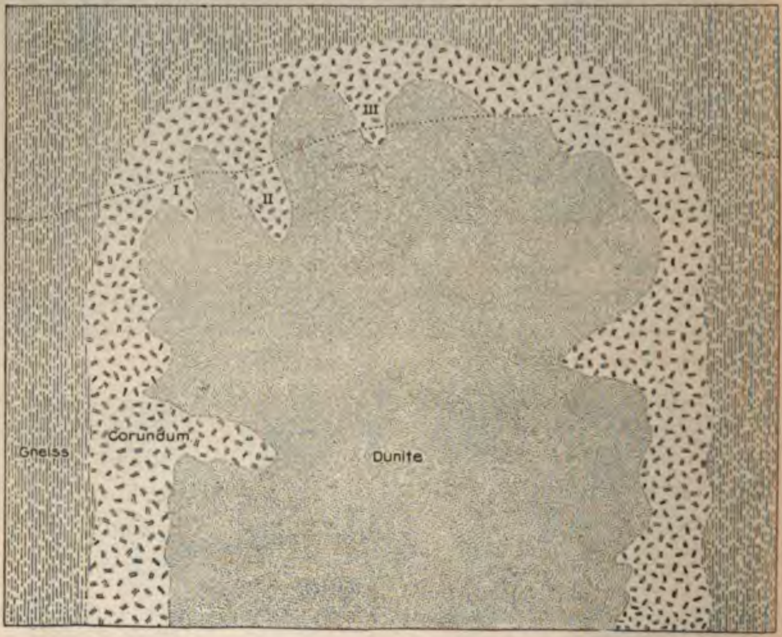

FIG. 105.—Ideal vertical cross-section of mass of peridotite soon after its intrusion into gneiss. (*After J. H. Pratt.*) The corundum is concentrated around the border of the dunite (exaggerated in the figure), forming sharp contact with the gneiss, but irregular ones with the dunite or peridotite, with interior veins (I, II & III).

Sapphires.—Of exceptional interest is the occurrence of corundum as gems. Ruby and sapphire of fair quality are found in the crystalline limestones of southern New York and northern New Jersey, and in similar limestones and marbles in Ontario, Canada, and Ariège, France, and in the dolomites at St. Gotthard. In New York and New Jersey the occurrence is near dikes or bosses of intrusive granite. The sapphires of Queensland, Australia, occur in gravels probably derived from basaltic dikes, which cut granitic dikes and in which some sapphires have been found. The sapphires of Burma, Siam, and Ceylon, the finest in the world, are also found in gravel, the source of which is, however, as a rule unknown. In Burma rubies are found in place in limestones. Sapphires, including rubies, of gem quality also occur in a number of localities in the United States, especially on Cowee Creek, Macon County, North Carolina, and in the Missouri River near Helena; and in Rock Creek, Granite County, Cottonwood Creek, Powells and Yogo Gulch, Montana. These occurrences are chiefly in gravels, though many of them have been traced to their origin in andesite dikes.

The bars of the Missouri River east of Helena, Montana, are systematically worked for sapphires. These occur in the gravels but appear to have been derived from dikes of andesite. Sapphire gems have also been found in the Corundum Hill Mine of Macon County, North Carolina, this being the only place in the United States where green sapphire or oriental emerald has been found. Sapphires have also been found at some other localities in North Carolina, and elsewhere in the United States.

Emery.—The impure form of corundum, known as emery, is found in the United States in abundance in only a few localities. These are Chester, Massachusetts, near Peekskill, Westchester County, New York, and Macon County, North Carolina. The Chester mines originally yielded the largest production of emery in the United States, but this position is at present held by the Peekskill mines.

The Chester emery occurs in a band of amphibolite in sericite schist, which extends almost entirely across the state from north to south. The width of the amphibolite averages only a few rods, but increases to three-fourths of a mile in the Chester region. The emery occurs on the eastern side of the nearly vertical band of amphibolite and is separated from the sericitic schist by a narrow band of amphibolite, from an inch or two to nearly 18 feet in width. Sometimes the amphibolite has been serpentinized. The emery deposit has the form of a vein which has been traced for a distance of nearly 5 miles though it is not always emery-bearing. Its width varies from a few feet to 10 or 12 feet, the average width being about 6 feet. Upon both sides of the emery there are usually developed thin seams of chloride, varying from 1 to 6 inches or more in width. More or less chlorite also occurs in the emery.

The emery varies from an almost pure magnetite to an intimate mixture of magnetite and corundum, which is sometimes coarsely crystalline. In the early days the deposit was mined as an iron ore.

The emery of New York State is associated with the norite rocks of the Cortland series. These deposits also vary in character from nearly pure magnetite to a mixture of this mineral with spinel and corundum. Often the deposits consist almost entirely of magnetite and spinel. In form the deposits have the character of pockets in the igneous rock.

The emery of North Carolina occurs in a decomposed material which appears to be that of a basic magnesium rock of igneous origin. An emery deposit also has been described from saprolitic rocks of Pittsylvania County, Virginia.

Extensive emery deposits occur in the province of Aidin in Asiatic Turkey. The emery is embedded in a bluish, coarse-grained to compact marble or limestone which rests upon mica slates, schists and gneisses. It appears to be confined to the marble where it occurs in pockets scattered irregularly through the rock, these pockets being sometimes 200 feet in length and 300 feet in width. The walls of the pockets are very irregular, the limestone walls jutting in and out. In color the emery varies from dark blue to purplish.

Emery has also been found abundantly on the island of Naxos and elsewhere in the Grecian Archipelago. It is embedded in white marble or, at Naxos, occurs in large blocks more or less mixed with the red soil.[1]

Phosphates

Apatite ($Ca(FCl).Ca_4(PO_4)_3$).—This mineral is widely disseminated as an original constituent of many igneous rocks, especially the feldspathic, highly ferro-magnesian ones. In these it occasionally forms a considerable percentage of the whole, as in the pyroxene-apatite-syenite of Finland. Sometimes it occurs in comparatively large, stout crystals or irregularly shaped, colorless anhedrons. It also abounds in metamorphic limestones, where its source is probably organic. Occasionally it occurs in veins. The apatite of Norway is regarded as of igneous origin and is especially abundant in schists and other metamorphic rocks.

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[1] For further details consult the Bulletin on Corundum and its occurrences and distribution in the United States, by Joseph Hyde Pratt, Bull. 269, U. S. Geol. Surv., 1906. Also A. E. Barlow, *Corundum*, Mem. 57, Geol. Survey of Canada, 1915.

Fluorides

Cryolite (Na_3AlF_6 or $3NaF.AlF_3$).—This salt occurs, according to Johnston, as a large body within granite at Ivigtut on Arksukfjord in West Greenland. Within the central part of the mass and through it, are scattered crystals and masses of quartz, siderite, galena, sphalerite, pyrite, chalcopyrite, and wolframite. The outer portion of the mass passes into the surrounding granite without distinct boundary, and contains quartz, feldspar, muscovite, fluorite, cassiterite, molybdenite, arsenopyrite, and columbite. It also occurs in granite in the Urals and at Pike's Peak, Colorado (Iddings).

NON-METALLIC SALTS, OTHER THAN SILICATES, IN VEIN AND CAVITY DEPOSITS

Veins are secondary or epigenetic deposits formed in preëxisting fissures (fissure veins) or in fissures formed simultaneously with the deposit which chemically replaces the country rock (replacement veins). Cavity deposits are irregular mineral masses in the rock, and they, like veins, may be formed in preëxisting cavities or by replacement. Cavities are often parallel to the bedding of stratified rocks, while veins as often cut them. Both yeins and cavity deposits may suffer secondary enrichment by concentration in them of additional material brought in solution from elsewhere. The material is brought to the fissure or cavity or the place of deposition either by waters or by vapors, the latter commonly of volcanic or fumarolic origin. The water may be descending water from the vadose or phreatic circulation, or ascending from magmatic sources.

The vein and cavity deposits of greatest economic importance are those which contain metallic salts or native metals. Veins of silicates, too, are common, and not infrequently veins of minerals other than silicates occur. The more common or economically important of these include the following minerals.

Oxides and Hydroxides

Quartz (SiO_2).—This occurs both in crystallized and amorphous form (chalcedony), in practically all types of rocks. In druses it forms geodes of amethyst and clear quartz, and as amorphous fillings of cavities it forms agates. Vein quartz is one of the most important gangue minerals of native gold and other metals and ores.

Diaspore ($AlO(OH)$).—This occurs in association with corundum and emery as vein material in various crystalline rocks in Europe and America. It has also been found to some extent as original (?) and secondary inclusions in igneous rocks.

Carbonates

Calcite ($CaCO_3$).—This salt is likewise common in veins and cavities, where it is frequently the gangue mineral of ores. It also occurs in cavities and druses as crystals, occasionally perfectly transparent (Iceland spar). Sometimes crystals of enormous size are found lining caverns which were at one time filled with water and so have the character of giant druses.

Dolomite ($CaMgCO_3$).—This occurs much in the same way as calcite does.

Strontianite ($Sr.CO_3$).—This occurs in cavities in limestones and other rocks, sometimes highly crystallized. More rarely it is found in veins.

Sulphates

Alunite ($KNa(AlO_2H_2)_3.(SO_4)_2$, or $K(AlO_2H_2)_3(SO_4)_2$).—This important ore of potash and of alum is found in veins and bedded deposits in many parts of the world, the latter being apparently alteration products of volcanic sheets.

What are regarded as true vein deposits of alunite, formed in open fissures, occur in the Tushar range near the head of Little Cottonwood Canyon near Marysvale, Utah. The main deposit forms a large banded vein, cutting the dacites and andesites of the range at a steep angle. The best exposure shows a thickness of the veins of 26 feet, of which 20½ feet are high-grade alunite, and 5½ feet quartz. Other openings show thicknesses of 8 to 20 feet. The extent and depth of the veins is undetermined.

Three varieties of alunite are noted in the veins: (1) coarsely crystalline, (2) fine-grained to dense, and (3) laminated. The first is the most common, pink to reddish in color, and forms large masses of columnar to platy crystals as well as small veinlets that cut the other two varieties. Its specific gravity is higher than the normal, being about 2.82, and it is practically pure, except for minute quantities of pyrite or limonite and silica (chalcedony and opal). The second variety is pink to white, and resembles porcelain when hard, and chalk when weathered. Impurities (pyrite, silica, kaolin) are at times conspicuous under the microscope. It is likewise distinguished by its high specific gravity. The laminated variety differs from the fine grained only in its shaly structure, due to shearing. The wall rock of the vein is altered for many feet on either side.

The veins are regarded as formed by heated solutions, probably of magmatic origin, which derived their mineral content from the crystallizing magma, but some of the potassium and aluminum was probably also obtained from leaching of rocks which carry potash feldspars, through which these waters passed. The sulphuric acid may also have been derived from the magmatic emanations, either as such or as hydrogen sulphide, which was oxidized at or near the surface to sulphuric acid. The deposition of the alunite is believed to have occurred in the upper cooler portion of the fissures, and the character of the vein is thought to change downward. The pure alunite portion of the vein is preserved only where erosion has not been too intense.[1]

Analyses of these alunites by the Federal survey gave the following compositions for the Marysvale deposits.

TABLE XCVII.—COMPOSITION OF MARYSVALE ALUNITES

	Coarsely granular, clear pink, best variety	Light pink, finely granular or nearly porcelaneous	Theoretical composition of alunite, Dana
Al_2O_3	37.18	34.40	37.0
Fe_2O_3	Trace	Trace	
SO_3	38.34	36.54	38.6
P_2O_5	0.58	0.50	
K_2O	10.46	9.71	11.4
Na_2O	0.33	0.56	
H_2O+	12.90	13.08	13.0
H_2O-	0.09	0.11	
SiO_2	0.22	5.28	
Total	100.10	100.18	100.0

On the western side of the Tushar Mountains occur other deposits of Alunite, of which one at Sheep Rock, near Beaver, Utah, has been studied in detail.[2] It is a bare-topped ledge of nearly circular form, about 900 feet in diameter, with a gently rounded summit, weathered in part into a cluster of rounded residual boulders which from their resemblance to sheep have given the region its name. The material is a nearly white Alunite rock, containing from 30 to over 70 per cent. of SiO_2. Unlike the deposits on the eastern side of the mountain at Marysvale, the Sheep Rock deposit is believed to have been wholly formed by the replacement of porphyry, with the result that the two minerals, alunite and quartz, were intimately mixed. The replacing material was, as in the former case, brought by hot, ascending solutions.

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[1] For further detailed descriptions and discussions of these deposits see B. S. Butler and H. S. Gale, Alunite, A Newly Discovered Deposit near Marysdale, Utah, Bull. 511, U. S. Geol. Surv., 1912; and G. F. Loughlin, Recent Alunite Developments near Marysvale and Beaver, Utah, Bull. U. S. Geol. Surv., 620-K, pp. 237-270, 1915.

[2] Loughlin, *loc. cit.*, p. 258.

Extensive deposits of alunite occur at Goldfield, Nevada,[1] where it is found as a soft white or slightly pink material, closely resembling kaolinite and, like that mineral, filling cavities in ledge matter or ore, and as an integral constituent of altered rocks (rhyolites, andesites, dacites). Both the feldspar phenocrysts and the ground mass have been altered to an aggregate of alunite and quartz. Diaspore occurs with it in subordinate amounts. The alunite is also abundantly associated with the sulphide ores, and in many cases intercrystallized with pyrite. Much of the material is natroalunite.

Other deposits in Nevada have been regarded as due to alteration of the rocks by hot, ascending, acid, volcanic, mineralized vapors. From the Rico Mountains, Colorado, Cross[2] has described alunite deposits which "can be explained only as the result of the attack of sulphurous agents . . . to be attributed to solfataric emanations of the Rico eruptive center in the period of waning igneous activity." Similar deposits of alunite in the Rosetta volcanic hills, 25 miles southwest of Canyon City, Colorado, are regarded by him as produced through the alteration of rhyolite by solfataric vapors or by waters containing such vapors in solution.[3] A rhyolite dike altered to quartz alunite forms the highest peak of the hills (Mount Robinson), which is due to resistance of the alunite to erosion. The percentage of silica in these deposits ranges from 65 to nearly 70. Diaspore occurs with the quartz and alunite.

One of the most remarkable deposits of alunite occurs in the parish of Bullah Delah, County of Gloucester, New South Wales.[4] It consists of a narrow mountain range about 3 miles long and having a maximum altitude of 900 feet. For a mile or more this ridge is composed almost entirely of alunite of greater or less purity. The beds form a steep anticline, dipping at angles of 80 to 83° in opposite directions, and rising as a sharp, almost perpendicular, crown of alunite for 400 feet above the talus covered sides. This crest is cut at intervals by saddles where transverse dikes of dolerite have partly weathered away.

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[1] F. L. Ransome, Geology and Ore Deposits of Goldfield, Nevada, Prof. Paper U. S. Geol Surv., No. 66, 1909, pp. 129–133.

[2] Whitman Cross and A. C. Spencer, Geology of the Rico Mountains, Colorado, 21st Ann. Rep., U. S. Geol. Surv., pt. 2, 1900, pp. 92–94.

[3] Whitman Cross, Geology of Silver Cliff and the Rosetta Hills, Colorado, 17th Ann. Rept., U. S. Geol. Surv., pt. 2, 1896, pp. 263–406.

[4] E. P. Pittman, Alunite or Alumstone in New South Wales, Rept. Geol. Surv. N. S. W., 1901, pp. 419–429. See quotation in Bull. 511, U.S.G.S., pp. 55-57.

Four varieties of alunite are found: (1) light pink, containing 1.7 per cent. of silica; (2) chalk white, containing 16.4 per cent. of silica; (3) purple, containing 19.5 per cent. of silica, and (4) granular, containing 39.5 per cent. of silica.

The alunite is regarded as formed by the alteration of trachyte flows which are interbedded with the Permic deposits, and which away from the mountain are for the most part unaltered. The Permo-Carbonic rocks with their interbedded trachyte lavas appear to have been folded into the sharp anticline, and subsequently, during the Tertiary, intersected in an east-west direction by a number of dolerite dikes. "These later volcanic intrusions were probably attended or followed by evolutions of steam and sulphurous acid vapors, which, acting upon the rhyolites, produced the alunite. Denudation in Post-Tertiary time removed the covering of soft sandstones, leaving the anticlinal arch of resistant alunite in relief."

The long-known deposits of alunite at Tolfa, Italy, are now regarded as due to alteration of pyritic trachyte veins in trachyte, by surface waters. They are noted in the next chapter (page 366).

Anhydrite ($CaSO_4$).—This is frequently formed as the result of solfataric action, and has been found in veins and irregular deposits in regions where such processes have occurred.

Barite ($BaSO_4$).—This occurs in veins and cavities in limestones, sandstones, and other sediments, and in igneous rocks which have been subjected to solfataric action. It also occurs in concretionary masses of crystals and sometimes as bedded deposits in sediments. It frequently forms an important gangue mineral in ore-bearing veins.

Celestite ($Sr.SO_4$).—This occurs in cavities and veins in limestones, etc., after the manner of barite.

Gypsum ($CaSO_4.2H_2O$).—This mineral is not uncommon in cavities and veins in limestones and other rocks. It occurs as crystals of selenite in veins and as plates cutting limestones in all directions. As satin spar, it forms veins of fibrous gypsum with the fibers pointing toward the center of the vein. As solid masses of alabaster, it occurs replacing corals and other organic structures in limestones. Extensive deposits of gypsum are believed to have been formed by deposition in veins and cavities, especially along faults. It also is a product of fumarolic action around volcanic vents, and in fissures, in lavas. It is common as a replacing deposit of limestone (see Chapter XVI).

Phosphates

Lazulite ($2AlOH.MgPO_4.FePO_4$).—This mineral is sometimes common in veins and pockets, occurring in sandstones or quartzites (Sweden, etc.) in clay-slate near Werfen, Salzburg, in Corundum, U. S., etc.

Apatite ($Ca(F.Cl).Ca_4(PO_4)_3$).—This mineral sometimes occurs in veins in granite, as on Long Island, Maine. It is more commonly a constituent of igneous and metamorphic rocks where it occurs in vein-like masses or pockets as in Canada.

Phosphorites.—The non-crystalline phosphates of lime occur sometimes in veins as in the Spanish deposits.

Nitrates

Niter (KNO_3).—As veins of more or less impure material of recent origin in rocks of some desert regions. (See discussion of nitrate deposits in western United States, *ante*, p. 298.)

Fluorides

Fluorite (CaF_2).—This mineral occurs in crystallized form in fissures and cavities often forming a gangue mineral for metallic ores, especially galenite and sphalerite. It is commonly a product of fumarolic or pneumatolytic action or gaseous exhalations. It is common in fissure veins in southern Illinois and adjoining districts of Kentucky, where it occurs in large bodies of unusual purity, which are extensively mined. The mineral is crystallized, and in druses and open spaces well-developed crystals are not uncommon. For the most part, however, the fluorite of this region occurs in great, vertical sheets or veins, clearly crystallized but not showing crystal form. Associated with it are calcite, quartz, barite, dolomite, and kaolin, all of these with the fluorite forming the gangue minerals of veins carrying a limited amount of galenite and sphalerite. These veins occur in fault fissures in the Mississippic limestones, but the fluorite is the only mineral mined at the present time. The source of the mineral has been thought to be disseminated grains of it in the limestones of the region. On the other hand, the presence of a number of dikes which cut the limestones of the region, indicates the presence of deep-seated, igneous masses from which fluorine-bearing gases and waters were derived. "The association of the minerals and the common phenomena of marked silicification of the hanging wall are interpreted as indicating deposition from heated, ascending solutions carrying fluorsilicates of zinc, lead, copper, iron, barium, and calcium. These are believed to have been broken up and precipitated by descending cold waters, which possibly also furnished the sulphur to combine with the metals, though it is not improbable that sulphur was an original constituent of rising solutions."[1]

Deposits of fluorite also occur in many other regions of the United States, especially in the Piedmont and Appalachian areas from Maine to Virginia, and in association with metalliferous veins in some of the western States. It also occurs in Central Kentucky and Tennessee and in druses in the St. Louis limestone at St. Louis. In the north of England (Cumberland), it occurs in the Mountain Limestone (Mississippic), where this is cut by dike rocks. Some of the finest and largest museum specimens of crystallized fluorite have been obtained here. Near Freiburg in Saxony, it occurs in veins and druses in gneisses, schists, and slates, cut by dikes of quartz-porphyry and by gabbro. Here, too, it is associated with sulphides of the metals.

Borates

Colemanite ($Ca_2B_6O_{11}5H_2O$).[2]—The extensive beds of Colemanite in the Tertiary beds of California which have generally been referred to playa or lake deposits, are regarded by Gale as more probably vein deposits, resulting from the replacement of the carbon dioxide of limestones by boric acid derived from neighboring volcanic sources. Associated with them are veins of gypsum, chiefly as selenite.

[1] H. Foster Bain, The Fluorspar Deposits of Southern Illinois, Bull. U. S. Geol. Surv. 256, p. 67.

[2] Gale, H. S., Prof. Paper U. S. Geol. Surv. No. 85, 1913, p. 3.

CHAPTER XVI

THE META-SALTS

Definition.—Under this name we include salts formed in situ as alteration or decomposition products, by the removal from or addition to substances from external sources, but not salts which have been leached from decomposition products and deposited elsewhere from solution or the state of vapor. This includes metasomatic processes, that is, the action of a solution or a vapor upon a preëxisting substance in such a way that as each particle of a mineral is dissolved, it is *immediately* replaced by a particle of another mineral of different chemical composition.

The chief salts thus included are gypsum, derived from limestones or from anhydrite; anhydrite derived from gypsum; and dolomite derived from limestones; siliceous and other replacement products; and the various aluminous residues due to decomposition of silicates. Other salts included here are those resulting from the reaction of salts of aqueous origin upon one another, the most significant examples of which are certain complex salts found in the deposits of Stassfurt and elsewhere.

ALTERATION OF LIMESTONES TO GYPSUM

On the Sinai peninsula and at several localities along the west coast of the Red Sea, sulphuretted springs acting upon the coral limestone of the coast alter it to gypsum. Wherever iron pyrites are enclosed in the limestones or in shales or other rocks associated with them, acid sulphates are formed by oxidation, and these, reacting upon the limestone, alter it to gypsum, either in part or throughout. Sometimes the alteration is such as to produce plates of selenite, which penetrate the rock in various directions. Such structures are not uncommon in the Lockport dolomitic limestone of western New York, where plates of selenite are sometimes found cutting in all directions across colonies of the coral *Favosites*. Frequently entire heads of ***Stromatopora***, which are common in some layers of this formation, are completely altered to a pure white alabaster. Small crystals of selenite likewise mottle some of the fine grained Devonic limestones of Michigan and elsewhere.

The Salina formation of New York State is characterized by an abundant development of gypsum, in beds interstratified with limestones, or with the rock salt. For the most part, however, the gypsum occurs in irregular masses, commonly with a flat base but rising in dome-shaped or broad columnar masses through the enclosing limestones, with layers of more clayey material or impure limestone passing through limestones and gypsum alike and marking the original stratification (see Fig. 106). Dana[1] has correctly interpreted these gypsum masses as resulting from the limestones which make up a part of this formation, the alteration being effected by the acid sulphate waters which abound in the formation and which have resulted from the oxidation of the iron pyrites in the rock. In some cases the strata overlying the gypsum beds are arched and broken, this appearing to be due to the swelling of the mass in the alteration process. The occurrence of gypsum in the dolomites overlying the salts at Goderich, Canada, is probably to be explained in a similar manner.[2]

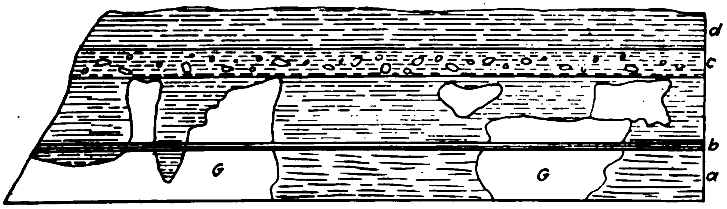

FIG. 106.—Gypsum (*G*) formed by alteration of limestone and other calcareous rocks. Saline formation of New York. (*After Hall.*)

Some of the gypsum, however, especially that intercalated with the salt layers in this formation, both in New York and Michigan and elsewhere, appears to be derived through the hydration of anhydrite which was an original deposit with the salt. These interbedded strata sometimes show a remarkable local folding and crumpling, an enterolithic structure produced by the swelling of the rock in the process of hydration (see beyond).

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[1] Dana, " Manual of Geology," 3d ed., p. 234.

[2] See T. Sterry Hunt, Geol. Surv. Canada Report of Progress, 1876–77, p. 221. Also Bull. No. 33, Bur. Soils, U. S. Dept. Agricul., 1906.

As will be more fully discussed in a subsequent chapter, the salt of the Salina formation is for the most part of connate origin, while layers of lime-sand and dust originating from the destruction of the limestones which surrounded the salt basins, were spread as clastic sediments over these salt accumulations. It is these limestone layers which have furnished much of the gypsum of this series by alteration.

The gypsum deposits of Nova Scotia have been attributed by J. W. Dawson[1] to the action of sulphuric acids, derived from volcanic sources on the marine limestones. Some of these gypsum deposits occur in the immediate vicinity of the vents of Triassic volcanoes and in these cases the gypsum is probably of secondary origin. It is not unlikely, however, that some of the late Palæozoic gypsum of this region was a direct deposit from marine sources.[2]

Double decomposition between calcium carbonate and solutions of magnesium sulphate or ferrous sulphate also produces gypsum, and such an origin for certain gypsums has also been advocated. Both barite ($BaSO_4$) and celestite ($SrSO_4$) may accompany gypsum deposits, resulting from the alteration of the carbonates of these substances by contact with acidulated waters from oxidizing iron pyrites, or by double decomposition with gypsum.

It must be remembered that salt deposits of connate origin are far less likely to be associated with gypsum of primary origin than are salts of marine origin. This is evident from the fact that sodium chloride is readily soluble, while the calcium sulphate, which may be left as an efflorescence by the evaporation of the connate sea water, is less likely to be redissolved, and if dissolved is likely to be redeposited in separate districts from those in which the salt is finally left. This would account for the relative poorness of desert salts in gypsum, as well as the lack of calcium sulphate in the waters of basins supplied mainly from connate sources (Great Salt Lake). The salt deposits of Lop Nor in eastern Turkestan are described as very pure, gypsum being absent, though some of the red beds of the plains surrounding the salt area were studded with gypsum crystals. If it could be shown that primary gypsum is as a rule absent from connate salt deposits, an additional means for the interpretation of the older salt deposits would be obtained.

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[1] Acadian Geology, 1891, p. 262.

[2] See Mich. Geol. Surv., Vol. 9, pt. 2, 1904. Kans. Univ. Geol. Surv., Vol. 5, 1899. Iowa Geol. Surv., Vol. 3, pp. 257–304. Bull. N. Y. State Mus., Vol. 3, No. 11, 1893. Bull. U.S.G.S. No. 223, 1904. See further: Cameron, Frank K., and Bell, James M., Calcium sulphate in aqueous solutions. U. S. Department of Agriculture Bureau of Soils, Bull., No. 33, 1906.

GYPSUM PRODUCED BY THE HYDRATION OF ANHYDRITE

When calcium sulphate is deposited under arid conditions it is frequently in the anhydrous form. Anhydrite is the common associate of many older salt deposits, it being the usual form of calcium sulphate in the Stassfurt and other such salt formations. It is probable that it is the normal form in which calcium sulphate is deposited from solutions high in chlorides, while gypsum is formed when the original solution is less saline. The alteration of anhydrite to gypsum takes place by a process of hydration, the anhydrous sulphate taking up two molecules of water. This process involves an increase in volume of from 30 to 50 per cent., and the swelling thus brought about becomes a factor in the deformation of the strata. Where thin anhydrite layers are enclosed in rock salt or other beds which are not affected by the alteration, the layers themselves will undergo deformation without appreciably affecting the enclosing rock. Thus local crumplings of layers and often intense foldings of the altered beds may be effected while the enclosing rocks retain their original structure. Such deformations are called enterolithic,[1] and they are well shown in some of the gypsum layers in the rock salt of New York.[2]

Alteration of anhydrite to gypsum is observed in process at Bex in Switzerland, where the change has extended to a depth of 60 to 100 feet, while below this unaltered anhydrite is found. Sometimes pieces of anhydrite are found, altered between the folia, or on the exterior, so that the transition from one to the other mineral can be traced. Where land slides have carried away the surface mass of gypsum, the freshly exposed interior is found to be anhydrite.

ALTERATION OF GYPSUM TO ANHYDRITE

By the dehydration of gypsum, anhydrite may be produced, but to what extent this process goes on in nature is not known.

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[1] A. W. Grabau, "Principles of Stratigraphy," p. 757.

[2] 15th Ann. Rept. N. Y. State Geol., p. 212, pl. IV.

Anhydrite as pseudomorph after gypsum has been found in the Triassic salt deposits at Sulz on the Neckar. From this G. Rose[1] argued that in nature gypsum is sometimes altered to anhydrite. Similar pseudomorphs of anhydrite after salt have been found at Hall in Tyrol.[2] Pseudomorphs of anhydrite after salt are frequently accompanied by the formation of dolomite. The more frequent formation of pseudomorphs of gypsum after salt, however, is never so accompanied.[3]

Anhydrite has, however, been produced in the laboratory by heating gypsum in a closed vessel with sodium or calcuim chloride.[4]

On heating gypsum to a temperature of 107°C. the hemihydrate known commercially as plaster-of-Paris is formed. The reaction is: $CaSO_4.2H_2O \rightleftarrows CaSO_4.\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$ (liquid). In the presence of NaCl, this change takes place at 76°C. and in the presence of magnesium chloride at 11°C.[5]

If anhydrite ever forms in nature by the dehydration of gypsum, a shrinking equal to from 30 to 50 per cent. of volume would occur, and this, in any extensive series of deposits, would have a decided brecciating influence on the enclosing rocks. We may, however, doubt if anhydrite is ever an important secondary product (see also *ante* p. 176).

ALTERATION OF LIMESTONES TO DOLOMITES

That many dolomites are secondary products due to alteration of limestones is generally recognized, though a number of dolomites are undoubtedly original deposits. That dolomite may result by chemical precipitations from solutions of the bicarbonates by alkaline carbonates at high temperatures, has been shown by laboratory experiments, such as those of T. Sterry Hunt. Dolomite has also been produced by the action of a solution of magnesium bicarbonate on calcium carbonate at 100° in a closed tube.[6] G. Linck has produced dolomite by adding calcium chloride to a mixed solution of magnesium chloride, magnesium sulphate, and ammonium sesquicarbonate, and gently heating for some time the amorphous precipitate which was produced. In nature, Linck believes that ammonium salts derived from the decomposition of organic material acting on solutions of the chlorides and sulphates in the sea water precipitate marine dolomite.

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[1] G. Rose, Über die Bildung des mit dem Steinsalz vorkommenden Anhydrite. Monatsber., d. Kgl Akad. d. Wiss. zu Berlin, 1871, Pogg. Ann., 1872, 145, 177.

[2] Haidinger Poggendorf. Ann., 1847, 71; 247.

[3] Vater, H., Sitzb. Berlin Akad. d. Wiss., 1900, p. 274.

[4] Hoppe-Seyler, *loc. cit.*

[5] Van't Hoff and Weigert, Sitz. ber., Berl. Akad., 1901, p. 1141.

[6] F. Hoppe-Seyler, Zeitsch. Deut. Geol. Gesell., Vol. 27, 1875, p. 509.

Magnesium carbonate is a constituent of the calcareous structures of a number of marine organisms, especially certain nullipores or calcareous algæ, and crinoids, which latter have been found to contain as much as 12 per cent. or over of $MgCO_3$. By subsequent leaching of the more soluble calcium carbonate, the rock formed from such organisms becomes relatively enriched in magnesium carbonate until the composition of dolomite is approached. In all cases where the mixed carbonates occur in the right proportion, heat and pressure may result in their combination to form dolomite. That a number of dolomitic rocks are of clastic origin, derived from the destruction of older dolomites under semi-arid climatic conditions, and the redeposition of the clastic material as magnesian lime sands and muds, has elsewhere been argued by the author.[1]

Although many dolomites are thus original deposits, the fact that many others are alteration products cannot be denied. Lime rocks in which the calcium carbonate is in the form of aragonite, as in the case of rocks formed from corals, appear to be more readily altered than those in which the lime is in the form of calcite. In modern coral reefs, rocks carrying 38.07 per cent. of magnesium carbonate have been found by Dana, and Skeats found the proportion of $MgCO_3$ as high as 43.3 per cent. This approaches closely the amount required for true dolomite, which is 45.7 per cent. The alteration here appears to be due to the action of sea water rich in magnesium, and probably concentrated in lagoons, upon the coral rock. In the deep borings on the coral reef atoll of Funafuti in the Pacific, the older coral rock between the depths of 698 and 1,114 feet ranged in its percentage of $MgCO_3$ around 40, the lowest being 38.92 and the highest 41.05 per cent. The coral rock nearer the surface was altered to a much smaller degree, and some of it not at all. Contrary results were, however, obtained from borings at Key West, probably because coral rock there played a less important part in the original construction of the limestones.

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[1] A. W. Grabau, "Principles of Stratigraphy," p. 760, also Grabau and Sherzer, Monroe Formation of Michigan.

The enrichment of limestones originally poor in $MgCO_3$ by leaching of the more soluble $CaCO_3$ or by the introduction of magnesium, is not, of course, confined to rocks still under the sea, but may be equally effected in the region of vadose circulation. Relative enrichment by solution of the lime carbonate is probably more effective here than the introduction of magnesium carbonate, although the latter has been observed to take place in a number of localities. Change from limestone to dolomite by leaching, implies, of course, a considerable shrinkage in volume, and this may be expressed by brecciation or other deformations in the enclosing rocks. Replacement of calcite by dolomite also involves a contraction to the amount of 12.3 per cent., and pressure may favor such a replacement. This seems to be suggested by the more frequent occurrence of dolomite in regions of tectonic disturbances.

THE RARER META-SALTS

Among the rarer meta-salts found in the deposits which have resulted from precipitation or by separation from marine or continental waters under concentration, a few may be mentioned. Among the salts of the Stassfurt series, thus formed, is loeweite ($MgSO_4.Na_2.SO_4.2\frac{1}{2}H_2O$), probably derived by dehydration from bloedite (astrakanite) ($MgSO_4.Na_2SO_4.4H_2O$) (Van't Hoff and Meyerhofer). Vanthoffite ($MgSO_4.3Na_2.SO_4$) appears to have been formed by a reaction between bloedite and sodium sulphate. Langbeinite ($2MgSO_4.K_2SO_4$) may be derived by various reactions from other salts found associated with it at Stassfurt, such as leonite ($MgSO_4.K_2SO_4.4H_2O$), Kainite ($MgSO_4.KCl.3H_2O$), Kieserite ($MgSO_4.H_2O$) and Picromerite or Schönite ($MgSO_4.K_2SO_4.6H_2O$). In the Punjab salt range of India langbeinite on exposure to the air has been found to gain 57 per cent. in weight by taking on water, and to change into a mixture of epsomite ($MgSO_4.7H_2O$) and picromerite ($MgSO_4.K_2SO_4.6H_2O$). Among the chlorides, Carnallite ($KMgCl_3.6H_2O$) may be formed by the direct union of bischofite ($MgCl_2.6H_2O$) and sylvite (KCl), with an increase of volume of 4.95 per cent. or it may give rise by dissociation to these two species, with a corresponding decrease of volume, a result probably more common under pressure, the carnallite being an original or primary deposit in the concentration of the mother liquor. All of these changes have been experimentally produced by Van't Hoff and his associates in their elaborate researches tending to elucidate the paragenesis of the Stassfurt salts.

The mineral Colemanite ($Ca_2B_6O_{11}.5H_2O$) forms from Ulexite ($NaCaB_5O_9.8H_2O$), in a sodium chloride solution, most readily at 70°C. Others of the minerals of Searles' playa will no doubt prove to be meta-salts when the paragenesis of these deposits is more fully understood. Alunite ($K(AlO_2H_2)_3(SO_4)_2$) is a secondary mineral in feldspathic rocks, altered by means of sulphur vapors. Periclase (MgO) is a product of metamorphism of magnesian limestones and dolomites, and occurs in lavas of Monte Somma, Vesuvius.

The following meta-salts are formed from the primary salts Kieserite and Carnallite, which are obtained from the condensation of sea water.

At 25°C.:

1. **Kieserite** ($MgSO_4.H_2O$) gives rise to:
   a. Hexahydrate, $MgSO_4.6H_2O$.
   b. Reichardtite, $MgSO_4.7H_2O$.
   c. Astrakanite, $MgSO_4.Na_2SO_4.4H_2O$.
   d. Thenardite, Na_2SO_4.
2. **Carnallite** ($KMgCl_3.6H_2O$) gives rise to:
   e. Sylvite, KCl.
3. **Kieserite and Carnallite** together give rise to:
   f. Kainite, $MgSO_4.KCl.3H_2O$.
   g Leonite, $MgSO_4.K_2SO_4.4H_2O$.
   h. Schönite, $MgK_2(SO_4)_2.\ 6H_2O$.
   i. Astrakanite, $MgSO_4.Na_2SO_4.4H_2O$.
   j. Glaserite, $K_3Na(SO_4)_2$.

At 83°C.:

4. **Kieserite** ($MgSO_4.H_2O$) gives rise to:
   k. Loeweite, $MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$.
   l. Vanthoffite, $MgSO_4.3Na_2SO_4$.
   m. Thenardite, Na_2SO_4.
5. **Carnallite** ($KMgCl_3.6H_2O$) gives rise to:
   n. Sylvite, KCl.
6. **Kieserite and Carnallite** together give rise to:
   o. Kieserite and Sylvite.
   p. Langbeinite, $2MgSO_4.K_2SO_4$.
   q. Loeweite, $MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$.
   r. Glaserite, $K_3Na(SO_4)_2$.

RESIDUAL DEPOSITS

Among the meta-salts we may class the purer residual deposits which have resulted from the decomposition of silicate rocks. Some of the more important of these are, besides the iron hydrates and the silica:

Kaolinite ($H_4Al_2Si_2O_9$).
Nontronite ($H_4Fe_2Si_2O_9$).
Hydrargillite (Gibbsite).($Al_2O_3.3H_2O$ or $Al(OH)_3$).
Bauxite ($Al_2O_3.2H_2O$) approximately.
Diaspore ($Al_2O_3.H_2O$ or $AlO\ (OH)$).
Alunite ($K(AlO_2H_2)_3\ (SO_4)_2$).
Magnesite ($MgCO_3$).

Products of Kaolinization.—Kaolinization is the process of decomposition of feldspathic rocks under ordinary atmospheric conditions in temperate climates, with the production of Kaolinite (hydrous silicate of aluminum) and Nontronite (hydrous silicate of iron). Kaolinite and Nontronite generally occur mixed, and with other hydrous silicates, etc. Kaolinite is stable, but Nontronite easily decomposes, yielding ferric hydroxide. Kaolinite is the chief product of the decomposition of the feldspar of igneous and metamorphic rocks, and is especially abundant in regions of granitic and gneissic rocks or where pegmatites occur. In some cases it is produced by pneumatolitic action, *i.e.*, the action of thermal waters and gaseous emanations. Where ascending thermal waters have produced the alteration, the change is most pronounced in the deeper regions, the rock nearer the surface being freshest, a condition just the reverse from that produced by atmospheric decay. Kaolinization by atmospheric weathering probably requires the presence of CO_2 and therefore takes place most readily where vegetation abounds and especially under moors. The reaction according to Van Hise is $2KAlSi_3O_8 + 2H_2O + CO_2 = H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3$.

The change of orthoclase feldspar to kaolinite is accompanied by a decrease of volume amounting to 54.44 per cent. The change to kaolin and quartz, as in the above reaction, involves a decrease in volume of 12.50 per cent.

Products of Laterization.—Laterization is the process of decomposition of feldspathic rocks which goes on in pluvial tropical regions and differs from kaolinization primarily in the formation of hydrous oxide of aluminum, *i.e.*, by the diminution or total disappearance of the silicic acid in combination with the bases. It is generally accompanied by the concentration of the iron oxides which give laterite a deep red color and the separation of silica, which goes into solution and is deposited elsewhere as agate or chalcedony. The minerals formed are the hydrous oxides of aluminum, Hydrargillite (crystalline) or Gibbsite (amorphous), and Diaspore, and the mixture of these in varying proportions known as Bauxite and which approximates to a ratio of water intermediate between that of the monohydrate Diaspore and the trihydrate Gibbsite. In general, laterite may be considered an impure or iron-rich variety of Bauxite. Kaolinite and quartz too may remain as impurities in the laterite, the former sometimes approximating 40 per cent. of the whole, while in other cases kaolinite has been found, constituting up to 50 per cent. or over of the mass. This is especially the case in laterites which have been transported as detrital material, during which process clay and quartz sand have become admixed. In the following table (from Clarke), the analysis of Gibbsite (*A*), Bauxite (*B*), and undisturbed Indian laterites (*C–F*) are given.

TABLE XCVIII.—ANALYSES OF GIBBSITE, BAUXITE, AND LATERITES

	A	*B*	*C*	*D*	*E*	*F*
	Gibbsite	Bauxite	Indian laterites formed in situ			
Quartz	......	......	......	......	10.52	
SiO_2	2.78	0.93	3.90	0.37	0.23	0.90
Al_2O_3	62.80	67.88	54.80	43.83	35.38	26.27
Fe_2O_3	0.44	4.09	13.75	26.61	34.27	56.01
MgO	0.03	.....	......	......	......	0.20
CaO	0.20	0.36	0.35	0.86	0.40	0.64
TiO_2	0.04	1.04	0.38	4.45	0.10	1.50
H_2O	33.74	26.47	26.82	23.88	19.00	14.39
	100.03	100.77	100.00	100.00	100.00	100.00

From these analyses it is seen that the laterite differs from Bauxite mainly in the high content of iron oxide. Bauxite has also been considered as a precipitate from thermal waters, the alumina brought in solution by the hot waters coming in contact with limestone. This mode of origin has been suggested for some of the French Bauxites which are associated with Cretacic limestones[1] and a similar origin has been suggested for some American Bauxites. On the other hand, the Bauxites of the northern Pyrenees are regarded as of residual origin by some recent French writers. The Bauxite rests upon Jurassic dolomites and is covered by beds of Aptien age. A part of the Jurassic and most of the Comanchic (Valanginien, Hauterivien, and Barremien) is unrepresented and it was during this interval, when the region was a land surface, that the Bauxite was produced. (For details see Chapter XXVII.) The aluminous rock, by the weathering of which this deposit was produced, appears to have been entirely destroyed, leaving the Bauxite to rest upon the old limestone surface beneath.

In the laboratory, crystalline Gibbsite or Hydrargillite has been produced by the passage of a current of carbon dioxide through a hot alkaline solution of aluminum hydroxide ($Al(OH)_3$) and from a saturated solution of aluminum hydroxide in dilute ammonia, by gradual evaporation of the ammonia.[2]

Diaspore has been found in metamorphic rocks and in nepheline-syenites, granites and basalt tuffs. Under certain conditions it is also formed as a decomposition product.

ALUNITE AS AN ALTERATION PRODUCT

Under the heading of salts in veins, alunite deposits were described, which resulted either as filling of fissures with material brought by heated solutions from below, or by alteration of volcanic rocks by solfataric action or by waters containing vapors in solution. Alunite occurs in a number of localities, however, as the alteration product of feldspars of the volcanic rocks in which the deposit occurs, by sulphuric solutions percolating from above, and formed by the oxidation of iron pyrites or other sulphides. Such is believed to be the origin of the powdery alunite of Cripple Creek, Colorado, and of those in the Horn Silver Mine, Beaver County, Utah.

The famous deposits of Tolfa, Italy, worked for centuries, are believed by De Launay[3] to have resulted from the alteration of pyritic trachyte veins by surface waters. The oxidation of the pyrite furnishes sulphuric acid, which alters the feldspar to alunite while in those places where pyrite is absent only kaolin is produced. The crystallized alunite and quartz forms a series of veins in the midst of the trachyte, of a lenticular character. As the veins are followed into the deeper portion of the rock the alunite begins to disappear, while pyrite makes its appearance.

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[1] H. Coquand, Bull. Soc. Géol. France, 2d ser., Vol. 28, 1870, p. 98, Auge, idem, 3d ser., Vol. 16, 1880, p. 345.

[2] A. de Schulten, quoted by Iddings, Rock Minerals, p. 572.

[3] L. De Launay, La métallogénie de l'Italie, Compt. Rend. 10th Int. Geol. Congr. Mexico, pt. 1, 1907, pp. 679–686 (partial translation in Bull. 511, U.S.G.S., pp. 51–55.)

MAGNESITE AS AN ALTERATION PRODUCT

Magnesite ($MgCO_3$) appears in nature in two forms (*a*) amorphous and (*b*) crystalline. Neither form occurs absolutely pure, there being generally an admixture of iron and aluminum oxides, of silica (especially in the amorphous variety) of lime carbonate, etc.

The dense amorphous magnesite is generally a derivation from serpentinized olivine-rich, igneous rocks, under the influence of surface waters, the carbon dioxide content of which dissolves the magnesium silicate of the olivine, etc., and precipitates it as carbonate. This has been designated white weathering by Krusch[1] and results in the production of a network of magnesite which penetrates the serpentine in all directions in root-like rarely regular veins, and veinlets. Sometimes, however, large vein-like masses up to 50 meters in length are produced as in the magnesite deposits of Macedonia but these too, generally occur in multiple association. The serpentinic rock is commonly brecciated the brecciation occurring at successive intervals. When first deposited the magnesite is in a gelatinous state and not infrequently plastic. The silica is generally separated out as quartz (opal according to some) along the borders of the veins, but sometimes forms a microscopic network intersecting the carbonate, which then appears high in silica.

Magnesite of this type occurs in Greece especially in the islands of Eubœa and Lennos. Sometimes the veins are from 15 to 18 meters thick and they have been worked to a depth of 50 meters. The magnesite of Eubœa is the purest so far found, containing up to 99 per cent. $MgCO_3$ though averaging on the whole as shown in Table XCIX on page 368.

In 1906 Eubœa produced 37,209 tons of raw, burnt magnesite and magnesite bricks. In Macedonia magnesite has been

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[1] Z. d. d. Geol. Ges., 1913.

TABLE XCIX.—COMPOSITION OF EUBŒA MAGNESITE

$MgCO_3$	94.46
$CaCO_3$	4.40
Fe_2O_3	0.08
SiO_2	0.52
H_2O	0.54
	100.00

extensively mined for many years. It generally occurs in veins from 40 cm. to more than 1 m. in width, one of them having been followed for more than 118 meters and to a depth of 50 meters. Other deposits of this type occur in Germany (Silesia) Austria, Italy, Serbia, the Urals of Russia, Africa, India (especially the Chalk Hills in Madras and Mysore), Queensland, New South Wales, South Australia, Tasmania and New Caledonia.

Crystallized Magnesite.—This occurs in association with the minerals of other salt deposits, etc., but also with decomposition products of a number of ores, and in the border zones of the serpentines as vein material. The magnesite deposits in the Carbonic graywackes of the Austrian Alps, have been regarded as metamorphic products from limestones, though they also, have been considered as thermal spring deposits. According to Redlich the limestone layers of the deposit were drawn out into lens-like masses during the mountain-making processes, after which solutions of magnesium bicarbonate changed them first to dolomite and later to pure magnesite. The excess of lime carbonate was removed in solution. The reactions are as follows:

1. $CaCO_3 + MgCO_3 = CaMg(CO_3)_2$
2. $CaMg(CO_3)_2 + MgCO_3 = 2MgCO_3 + CaCO_3$

This interpretation is supported by the almost universal presence of dolomite. It has been very generally applied to the occurrence of crystalline magnesite in sedimentary deposits. The production of the Alpine magnesite is believed to be associated with diabase and porphyry eruptions (Redlich) or with the formation of granitic laccoliths (Weinschenk).

The deposits at Veitsch in the Austrian Alps (between Wiener Neustadt and Tirol) are the largest of this type, but owing to impurities there is a loss of 60 to 70 per cent. of the material mined. The annual production here is about 100,000 tons, the total annual production of the Austrian Alps being about 150,000 tons. In Hungary magnesite beds are found in several districts especially in the Comitat Gömör, where at Lubenz it is quarried in six levels each about 10 meters high. The total Hungarian production lies between 25,000 and 30,000 tons, of which 3½ tons furnish 1 ton of calcined magnesite.

In Spain magnesites of this type are found in the lower Cretacic formations associated with limestones and dolomites. In Sweden magnesite occurs as lenses and layers in chlorite and amphibolite schists and encloses dolomitic masses. In the Paris basin deposits of magnesite are associated with gypsum. These may have a different origin.

CHAPTER XVII

DEFORMATION OF THE SALT BODIES

All salt deposits are subject to deformation and alteration (metamorphism) partly in themselves and in part in connection with the disturbances and deformation affecting the enclosing strata. As a rule only the most recent deposits are free from disturbances, but even these may suffer deformations at times. The two types of deformation which may affect the salt body are (1) those due to external causes (exogenetic) and (2) those due to internal causes (endogenetic).

TECTONIC STRUCTURES

Exogenetic Deformations.—These are primarily due to orogenic disturbances. In general, salt bodies thus deformed partake of the characters of other disturbed rocks, the bedded salts become inclined in position or entire salt masses may be thrust over younger strata as appears to be the case in some of the older Tertiary salt deposits of the Carpathians. In the Alps the salt body has often been placed in close juxtaposition to younger beds by such thrusting, leading to an erroneous determination of the stratigraphic relations of the salt body. Intense deformation by folding may result from strong compression, this being brought out by the interstratification of the salt body with the layers of gypsum or of mother liquor salts. Such deformation is shown in the salt deposits of the Cardona region in northeast Spain, but it can not be positively stated how much, if any, of this folding is due to tectonic causes and what part is produced by deformative movements within the salt body and due to endogenetic causes.

On the western and northern borders of the Harz, where Tertiary disturbances were very profound, the Permic salt deposits show steep dips, faults and underthrusts. Thickening and thinning of the salt mass and mother liquor layers, tongue-shaped lenses, occasional abrupt pinching out of layers and strong contortions (Salz-krampf) are characteristic of the occurrences here.

These have been fully described by von Koenen,[1] K. Beck,[2] G. Geinitz,[3] R. Lachmann[4] and others.

The Haselgebirge.—One of the most marked effects of external deformative agents upon the salt body, is the formation of a mixture of salt, gypsum, and clay to a more or less intimate extent, so that they form a semi-homogeneous rock mass. This is extensively the case in Triassic Salt deposits of the Alps where intense deformation has taken place since the deposition of the salt. The resulting product is known as *Haselgebirge* and it is the common type of salt-producing rock in the Alpine region where pure salt beds are much less common.

The salt is obtained from the Haselgebirge by processes of leaching (see further Chapter XXVI). The action of exogenetic forces in the formation of the salt domes is discussed beyond, under the caption of complex deformations.

ENDOGENETIC DEFORMATIONS

Under this division are generally classed the deformations resulting from the swellings of the salt body by recrystallization or by absorption of water or otherwise. Here belong the complimentary changes due to loss of water and consequent shrinking, as in the case of the change of gypsum to anhydrite, which involves a decrease of volume of 38 per cent. Collapse and brecciation of the formation as the result of partial or complete solution of a salt body, may also be mentioned here.

Enterolithic Structure.—One of the most marked internal deformations noted in salt bodies is the serpentine character of some of the included layers, especially those of the mother liquor salts. These deformations are often extreme, the layers becoming in places discontinuous and presenting the character of isolated stringers or breccia-like fragments in the enclosing salt. The following illustration from Everding represents such a deformation of Kieserite ($MgSO_4.H_2O$) in carnallite ($KMgCl_2.6H_2O$) from the Berlepsch shaft near Stassfurt (Permic salt deposits). (Fig. 107.)

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[1] Von Koenen Wirkungen des Gebirgsdruckes im Untergunde von tiefen Salzbergwerken. Nachrichten Kgl. Gesellsch. Wissensch. Göttingen. Math. Physk. Klasse, 1905, p. 17.

[2] K. Beck, Untersuchung des Salzgebirges an der oberen Aller. Zeit. für prakt. Geologie, 1909, p. 25.

[3] G. Geinitz, Salzlagerstätten von Jessenetz. Mitteil. Mecklenb. Geol. Landesanstalt. Rostock., 1905, p. 1.

[4] R. Lachmann Autoplaste Formenelemente, etc., *loc. cit.*, Salz-Auftriet. Kali Bd. IV, Heft. 8. 9, pp. 22–24, 1911.

The remarkable fact to be noted here is the undisturbed character of the carnallite layers which enclose the deformed Kieserite and the similar undisturbed character of the rock salt layers which alternate with the carnallite beds. It is evident that the disturbing force here affected primarily the Kieserite layers, and that it consists in an increase in extent of these layers which could only be compensated for by folding, while the carnallite otherwise unaffected by this force, became readjusted to this disturbed condition of the enclosed layers. Arrhenius holds that the forces which have brought about this peculiar deformation, are evidently of very local character, and confined to the respective carnallite layers.[1] Deformations of this type are among the most marked structures of many of the salt deposits of North Germany, where they are often most strikingly shown in the salt mines by virtue of the bright colors of many of the disturbed layers. They belong to the general type of structure called by German geologists "Gekröse structure" for which the equivalent English term is *enterolithic structure*, so named on account of the resemblance of some of these foldings to the convolutions of the intestinal tube in human anatomy.[2] Deformations of this

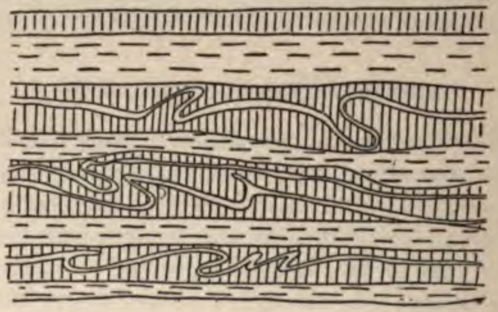

FIG. 107.—Section in the Berlepsch shaft near Stassfurt, showing the enterolithic deformation of Kieserite layers (white) in carnallite layers (vertical lining). The latter and the rock salt layers (horizontal dashes) are apparently undisturbed. (*After Everding.*) Scale, approx. 1:35.

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[1] Arrhenius, Svante, 1912, Zur Physik der Salzlagerstätten. Meddelanden från K. Vetenskapsakademiens Nobelinstitut Bd. II, No. 20, pp. 7–25.

[2] "Principles of Stratigraphy," p. 757–759, 788.

type are, however, not confined to mother liquor salts. They are shown in the salt and gypsum layers of the New York Siluric salt deposits where tectonic disturbance is absent. Indeed, they are found in other rocks as well, notably in the fine-grained clastic limestones (calcilutytes) such as those of the Niagaran of New York State and the Muschelkalk of Germany, from which latter formation the structure was originally described. In that case it has been held by Koken and others, that the deformation was due to the pressure of overlying formations, and the consequent squeezing out of the more plastic beds in some, and their compression into folded masses, in other portions of the bed. A similar origin has also been advocated by some for these structures in the German salt domes, while still others would refer them entirely to tectonic disturbance, *i.e.*, the action of the exogenetic forces.

COMPLEX DEFORMATIONS

Deformations due to a combination of causes probably in part tectonic and in part internal (endolithic) appear to have given rise to a type of structure common in the salt deposits of many regions. These are the *Salt domes*, the problem of the origin of which has given rise to an extensive controversial literature, some authors considering them as wholly due to tectonic forces, while others lean more strongly to an endolithic cause as the chief, if not the only, factor in their production. This subject has been treated at considerable length by G. D. Harris who has studied especially the salt domes of Louisiana. F. F. Hahn has summarized the discussion of the similar structures of the North German and other salt domes in the study of which many eminent foreign geologists have taken part. This type of structure was according to Hahn, first described by F. A. von Alberti,[1] who named them "acromorphs" a term designating wart-shaped excrescences. They have also been called uplifted horsts (Aufpressungshorste[2] and ekzemas.[3]) More recently the problem has again been attacked by G. Sherburne Rogers, who reviewed the various theories of origin and points out the weaknesses inherent in most of them.[1]

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[1] F. A. von Alberti, Hallurgische Geologie, 1852.

[2] E. Harbort, Geologie der nordhannoverschen Salzhorste., Monatsberichte d. deutschen geologischen Gesellschaft, 1910, p. 334.

[3] R. Lachmann, Autoplaste Formelemente im Bau der Salzlagerstätten Norddeutschlands, Ibid., p. 114.

THE SALT DOMES OF AMERICA

Structural Characters of the Salt Domes of the Gulf Region. In Louisiana[2] and Texas and on the Isthmus of Tehuantepec, Mexico, in the Gulf of Mexico region, the rock salt occurs in island-like masses within the enclosing rock, these islands often forming more or less dome-like elevations, and commonly restricted to approximately circular or oval areas, of varying extent.[3] Examination of the surrounding rocks indicates that these have been disturbed in the vicinity of the salt mass, *i.e.*, all around its periphery, the beds being commonly steeply inclined or even vertical, while a short distance away they assume their normal horizontal or slightly inclined position. Borings in the salt mass and on their periphery have shown that the salt is of great vertical but limited horizonal extent, that it rises indeed in a plug-like manner through the enclosing rocks and extends to an unknown depth. The typical surface expression of such domes is shown in the following two maps (Fig. 108, 109).

The enclosing strata range from recent alluvial sediments to beds of Cretacic age, which latter, when present, appear next to the periphery of the salt mass. These Cretacic beds represent about the horizon of the Nacatoch marls or Anona chalk of the Gulf Cretacic series (see Chapter XXIX).

The region in which these domes occur is one of extensive faulting, though the displacements are probably of no great extent, the faults being rather a series of pronounced fracture lines which penetrate the Tertiary and Mesozoic strata of the region. There is also some slight deformation expressed in broad synclines. Two sets of fault lines are recognized crossing each other approximately at right angles. These extend in general, northeast-southwest and northwest-southeast, respectively. It is at the intersection of known fault lines that the domes are located and Harris believes that "if all the faults in the beds beneath the Tertiary were located, domes would be found to occur mainly at the crossing of such fault lines"[1] (Fig. 110).

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[1] G. Sherburne Rogers, Intrusive Origin of the Gulf Coast Salt Domes, Economic Geology, Vol. XIII, No. 6, pp. 447–485, 1918. I take this occasion to record my appreciation of the character and great ability of this, my former student and valued friend, whose tragic death while engaged in exploration in South America has been a severe blow to all who knew him. A. W .G.

[2] G. D. Harris, Carlotta Maury and L. Reinecke, Geol. Surv., Louisiana Bull. 7, 1907, pp. 5–83.

G. D. Harris, The Geological Occurrence of Salt in Louisiana and East Texas, Economic Geology, Vol. IV, pp. 1–34, 1909.

[3] The more important of these domes are described in detail in Chapter XXXVII.

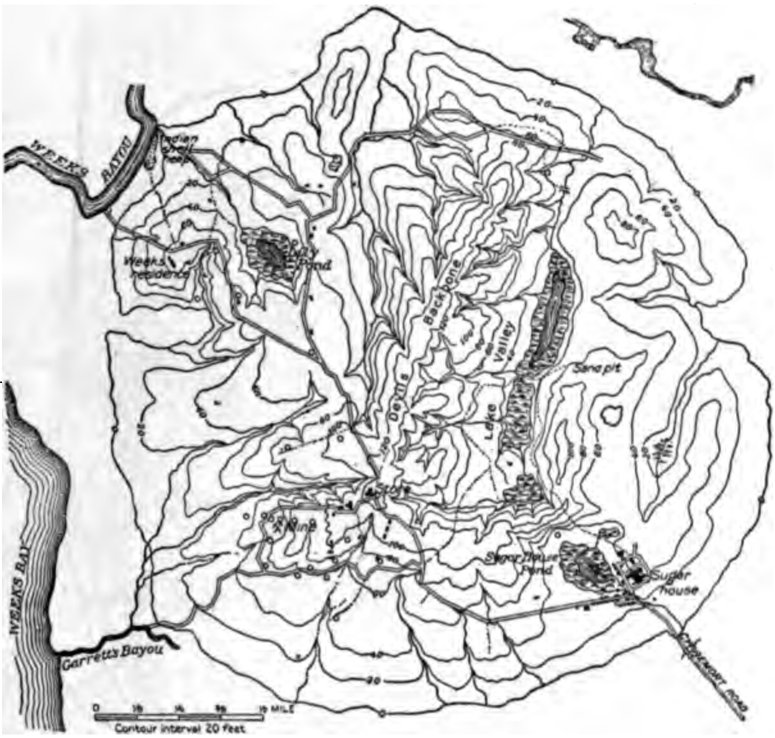

FIG. 108.—Topographic sketch map of Grande Côte (Week's Island), La. (*After A. C. Veatch.*)

Origin of the Domes of the Gulf Region.—Formerly these domes were looked upon as hills of circumdenudation left upon the old Cretacic land surface and surrounded by younger sediments, but the deformed character of these younger sediments near the domes and the fact that salt hills would scarcely remain as peaks above a land surface of erosion in a moist climate, has led to the abandonment of this hypothesis. It is now recognized that these salt masses have risen or been forced up through the enclosing strata which were deformed correspondingly. The forces appealed to as raising these masses have been various, such as gas-pressure, water under tremendous pressure, deep-seated igneous plugs, etc., but the detailed study of the deposits has revealed the inapplicability of all of these forces in the region in question.

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[1] *Loc. cit.*, 1909, p. 21.

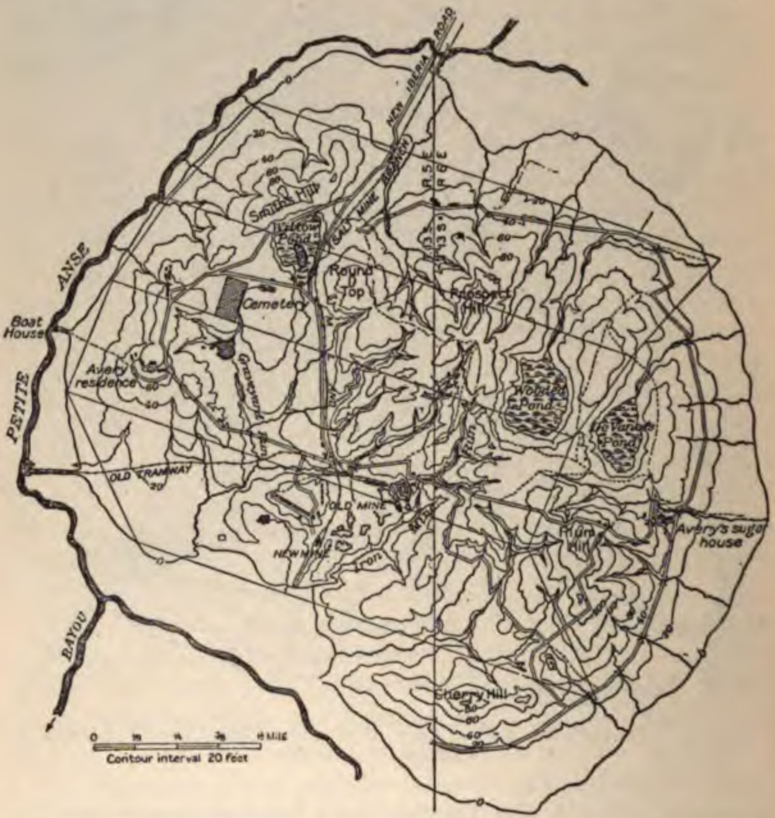

Fig. 109.—Topographic sketch map of Avery Island (Petite Anse), La. (*After A. C. Veatch.*)

Harris concludes that waters arising from great depths under hydrostatic pressure, and of considerable temperature along the points of intersection of the fault lines, brought the salt in solution from the older deposits, and permitted them to crystallize out as the waters reached levels of lower rock temperature. "Cooling normally at the rate of 1°C. for every 90 feet of ascent, a point would be reached where the solution, if saturated at a high

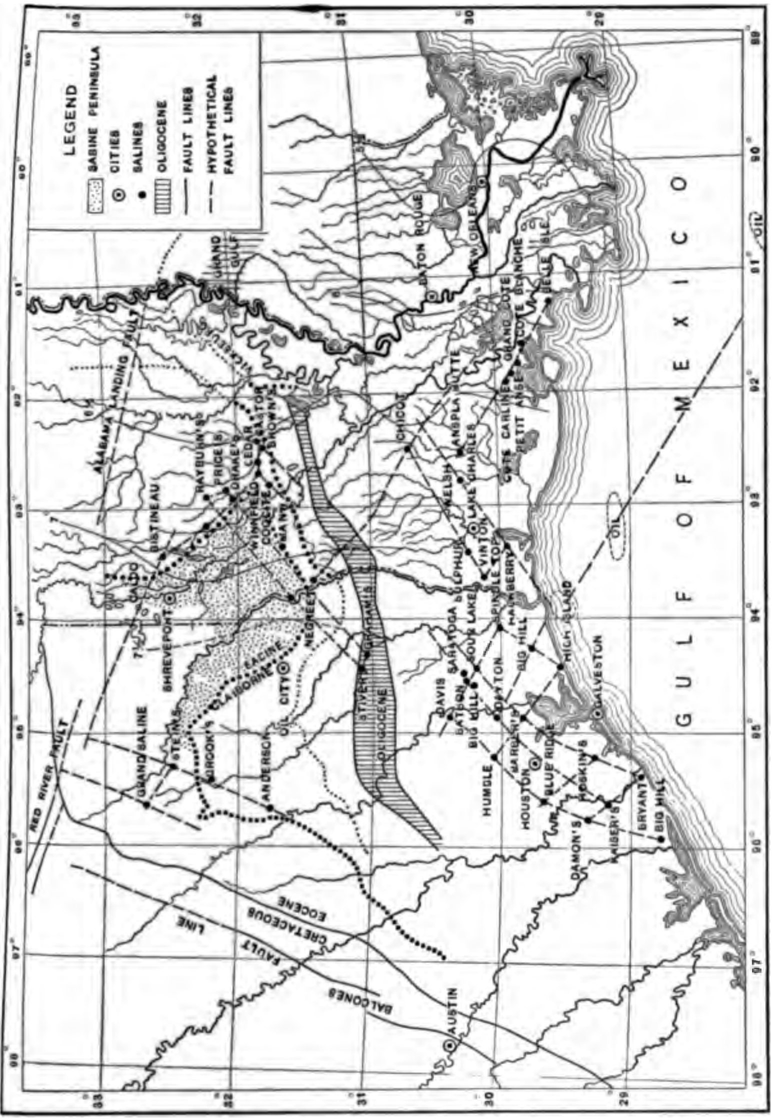

FIG. 110.—Sketch map showing the geology of part of Louisiana and Southeast Texas, with the locations of the salines and their probable relation to the structure. (*After Harris.*)

temperature, could no longer retain all its salts. Precipitation would begin rapidly at first * * * * but, decreasing slowly as cooler surface temperatures are reached."

Crystallization would accompany precipitation. Assuming that the pressure exerted by growing crystals is, in general, the same as the crushing strength of these crystals, which Harris has shown for a four inch cube of salt to exceed 50,000 lb. and which Tournaire has found for a cubic centimeter of such salt to range from 332 to 461 kilograms, Harris concludes that the growing salt mass could lift from 3,000 to 4,000 or even 5,000 feet of the incoherent Quaternary clays and sand which overlay the region of faulted Tertiary and older strata. The following set of figures from Harris shows this conception of the formation of the salt domes by the pressure of the crystallizing salt from the rising solution (Fig. 111). In No. 1 the older fractured strata are shown overlain by younger beds; No. 2 shows the crystallization of the salt in this fissure, and the slight arching at the surface accompanied by a condensing of the incoherent surrounding beds. "At first the salt core would be a slender pencil-like cone. By rapid growth at the base the apical angles would become greater and greater. The exact shape of the base of the cone would depend on many things, among which would be the comparative thermal conductivity of the salt core and the surrounding subjacent materials. Crystals formed on the base of the cone would give the whole mass an upward movement like a pelelith.[1] The apex of the cone would soon be above the isogeotherm where salt deposition is possible, and being of very limited lateral dimensions, it would be dissolved by circulating underground fresh waters. However, the compacting slickensiding of the deposits about the lower main part of the cone would tend to debar the close approach of fresh waters, and yet leave a suture line for the ascension of brines. So long as the supply of salt water lasted, the salt core would continue to grow and rise. But movements along the various fault lines might at any time shut off the supply of brine. Other solutions might be forced up through the channels formerly conducting salt waters. We note in the domes, next in importance to rock salt, gypsum, limestone, dolomite, indurated calcareous and siliceous lenses of varying shapes, and dimensions. Sulphur even alternates with gypsum layers. Oil and gas are found wherever some dome forming material has produced the proper structure to concentrate

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[1] A term applied to the rock mass pushed up from below as in the case of the "spine" of Mont Pelée.

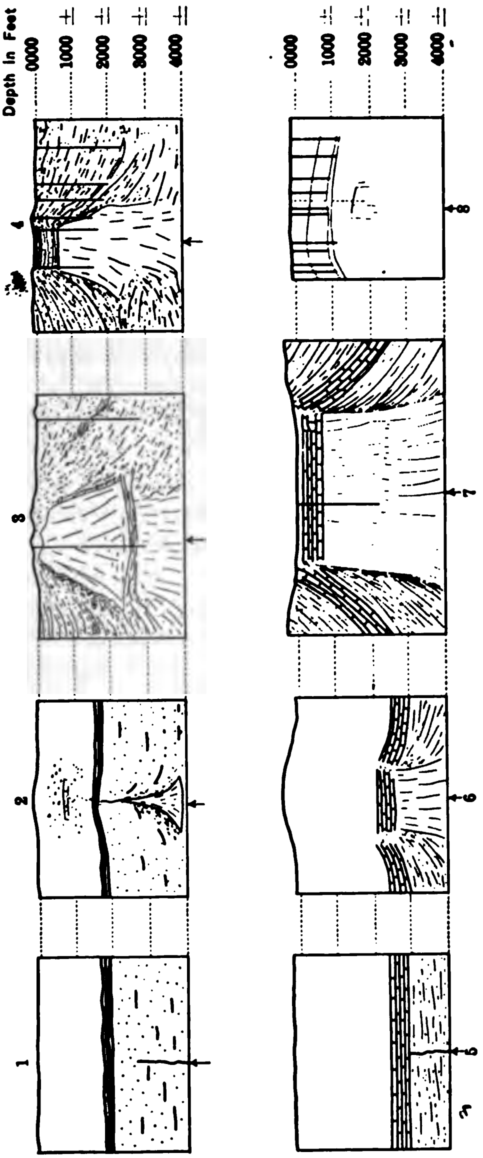

FIG. 111.—Figures representing G. D. Harris' conception of the origin of dome structure by crystalline growth. (*After Harris.*) (*For description see text.*)

and retain such substances. In an ordinary salt cone there should be growth not only at the bottom but also on the sides.

The ascending saline solutions would naturally vary somewhat as slight movements took place in the deeper lying beds below, and northward from any dome forming area.[1] These variations would be apparent in the salt as nearly vertical streaks or layers when the mass is exposed in the huge chambers of the salt mines. These streaks then, may be regarded as layers of exogenous growth rather than ordinary bedding planes highly inclined."[2]

Fig. 111, No. 3, represents a hypothetical section of the dome known as Petite Anse in Louisiana, (Fig. 109). This Harris considers to represent a case where the entire region has risen and the dome was truncated by erosion, though the salt was mainly preserved from the attack of fresh ground waters by the dense layers about its sides. In this dome a second salt mass has been reached by the drill. This is of later origin developing after the growth of the first has stopped, by exposure to the surface. Fig. 111, No. 4 shows the main structural features of Anse la Butte, another Louisiana dome. Two wells penetrate the truncated cone from 600 to 1,800 feet. Others enter the cone lower down. One penetrates a secondary salt mass before the porous oil stratum is reached. Harris regards this second mass as having been formed from a saturated solution of waters above the truncated cone while seeking a lower level, the solution meeting a heavy gas pressure and precipitating salt in consequence. Oil and salt water in this region show a temperature of 130° and 132°F. and gas bubbles continuously about the edges of the flat swamp area surrounding the dome.

Nos. 5 to 8 in Fig. 111 illustrate Harris' conception of salt dome formation where there is a comparatively thick, rigid layer above the salt forming locus. Nos. 5 and 6 are purely hypothetical. No. 7 is a section of Drake's Salina in northern Louisiana, which lies in the midst of Eocenic sands and clays and has a diameter of about a mile. Around it occurs a circle of brine springs. In the center, salt was encountered at 900 feet and gypsum at 2,300 feet, the very bottom of the test well. An old test well, reported from the right-hand side of the section is said to have passed through 1,100 feet of limestone. Cretacic sandstones at high angles occur on the left side of the section.

No. 8 shows the Spindle Top dome where the surface layer has been arched rather than broken, and lifted bodily. The salt is covered by a layer of gypsum, a very general mode of occurrence in Louisiana and Texas. This gypsum is regarded as secondary, deposited from the solution in proportion as the NaCl content of the water diminished, and its power to hold $CaSO_4$ in solution failed correspondingly. The extent of upward movement in these salt domes is shown by the presence of the older strata around their margins in regions where they normally lie several thousand feet below the surface. Thus the Cretacic strata in some sections of this region are covered by 1,000 feet of Eocenic, 1,000 feet of Miocenic, and at least 1,500 feet of Quaternary, indicating a minimum uplift of 3,500 feet.

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[1] The outcrops of the strata, lie successively to the north in this region and surface waters would there enter the porous strata.

[2] Harris, *Loc. cit.*, 1909, pp. 23–25.

This method of origin of the salt domes has been seriously questioned by G. S. Rogers[1] who regards the salt plugs as offshoots of deep-lying bedded deposits forced upward by tectonic agencies along lines of weakness. He admits the possibility of deep-seated batholithic intrusions as furnishing the pressure which was relieved by the rising of the plastic salt beds, and also considers the possibility of part of the pressure being due to the weight of the overlying strata. In the absence of direct proof of any intrusive activities in these regions in comparatively recent geological time, and because his calculations indicate that the weight of the overlying sediments is inadequate to produce the observed results, he appeals to lateral pressure in the deep lying consolidated sediments as the cause of deformation. The effects of such deformation would be less marked or even entirely wanting in the largely unconsolidated Tertiary and Quaternary deposits.

In support of his contention that purely tectonic forces are largely responsible for the formation of the salt domes, he cites the results of experiments on the behavior of salt under differential pressure, where the salt acts as a highly plastic substance being readily deformed, and if shattered welded again by pressure to a transparent mass. He adduces evidence of flow structure and pronounced contortions comparable to those of ancient deformed crystalline schists in the salt bodies, the elongation of the salt crystals in a vertical direction, the increase in the steepness of the flanking rocks with depth, such steepness rising to 60° or over, and the occasional presence of masses of apparently older rock carried up with the salt body. Increase of temperature with depth, and the presence of moisture in the salt, would enhance its plasticity and so diminish the required pressure. The capping layers of anhydrite, gypsum and limestone, he regards partly as material brought up with the salt and in part as probably due to subsequent activities of the ground waters.

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[1] *Loc. cit.*

Age of the Gulf Region Domes.—The age of the original salt beds, when their presence has been assumed by writers on these domes, is generally referred to the Palæozoic. Harris regarded them as possibly of Siluric age, Rogers favors, with others, a Permic age, though he considers the possibility of a Mesozoic age. As will be more fully shown in the stratigraphic chapters (Vol. II) the conditions for the formation of marine salts were most favorable in these regions in Jurassic and perhaps Comanchic time, and of continental salts in Triassic time, and the probability, that the original salt beds from which these plugs are derived was of early Mesozoic age is very strong. We have, however, as yet no definite proof that these salt deposits were of marine origin. This will be more fully discussed in Vol. II.

SALT DOMES OF EUROPE

Structural Characters of the North German Salt Domes.[1]—The North German salt deposits lie chiefly in the Permic and in the middle Triassic and they are described at some length in Chapters XXIV and XXVI. They are of especial importance on account of the occurrence in them of the mother liquor salts, among which the potash salts take the first rank from an economic viewpoint.

These salt domes of Germany[2] extend from the Elbe westward through middle and northern Hanover and Brunswick. They all pierce the thick younger formations in relatively small and isolated areas and are themselves covered by a thin blanket of the latest formations. The surrounding strata are all strongly uplifted and distorted, dipping away from the salt core which has the form of a plug with steep or vertical sides and round, oval or irregular section. Only a few hundred feet away from the salt core, the enclosing strata resume their normal, nearly horizontal position deeply burying the subjacent salt deposits.

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[1] H. Stille Aufsteigen des Salzgebietes. Zeitschrift für praktische Geologie Vol. XIX, p. 91, 1911.

O. Grupe, Zechsteinformation und ihr Salzlager im Untergrund des hanoverschen Eichsfelds. Zeitschr. für praktische Geologie, Bd. XVII, 1909, E. Harbort, *loc. cit.*, p. 185.

R. Lachmann, Autoplast. Formelemente, etc., *loc. cit.*

———Salzauftrieb, *loc. cit.*

———Salinare Spalteneruption gegen Ekzemtheorie, Monatsber. deutsch. geol. Gesellschaft, 1910, p. 579.

F. F. Hahn, "The Form of Salt Deposits, Economic Geology, Vol. VII, No. 2, pp. 120 to 135, 1912.

[2] In the discussion of these German salt domes some of which I had the opportunity of studying underground, under the guidance of Dr. Johannes Walther, I have followed closely the summary given by my friend and former associate Dr. F. F. Hahn, who carried on these studies while curator in my laboratory, and with whom I have had frequent discussion on this subject. His fall in the Great War has robbed me of a valued friend and science of a brilliant worker.

The salt mass of the dome is likewise much disturbed by cross foldings and intertwistings, often to such an extent that identification of the successive layers is impossible.

The following section of the Benthe-Horst about four miles from Hanover, illustrates the structure of such a dome[1] (Fig. 112). This is formed of the Permic salt mass but lies in the midst of normal lower and middle Triassic strata, while Oligocenic and younger beds cover its eroded surface. The bedding of the core is almost vertical, and it lies in the center of a strongly compressed anticline. It shows the normal succession of salt layers for the Permic deposits (see Chapter XXIV) but the layers are strongly crumpled and distorted. The salt is covered with a horizontal layer of residual gypsum.

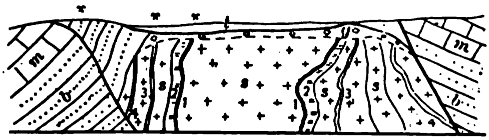

FIG. 112.—Section across salt-dome of Benthe scale 1/50,000. *t*, Oligocenic—Pleistocenic; *g*, Residual gypsum; *m*, Muschel-kalk (middle Triassic); *b*, Buntsandstein (lower Triassic); *s*, Permic rock-salt with (1) Hart-salt, (2) Principal anhydrite and gray salt clay, (3) Sylvinite, (4) Red salt clay. (*After H. Stille, Z. f. pr. Geol.*, 1911.)

About 20 miles southeast of Bremen lies another salt dome the salt of which is mined in the "Aller Nordstern" shaft near Verden[1] of which the following figure gives a section. (Fig. 113.)

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[1] Stille, H. Zeitsch f. prak. Geol., Vol. XIX, 1911, p. 91.

Ibid., Alter der deutschen Mittelgebirge. Centralblatt f. Mineralogie, vol. 1909, p. 270.

Ibid., Jahrb. Preuss. Geol. Landesanstalt, 1903, p. 296, 1905, p. 103.

Ibid., Mitteldeutsche Rahmenfaltung. 3 Jahresber. niedersæchs. Geol. Vereins, 1910, p. 14.

Ibid., Faltung des deutschen Bodens und des Salzgebirges. Kali, Vol. 5, 1911, Heft 16, 17.

The salt here lies at a depth of 350 feet and the borders of the dome are flanked by nearly vertical beds of Triassic strata. As in the other case cited, the salt, which is also of Permic age, is covered by a residual layer of lime sulphate (anhydrite in this case) and over this arched strata of upper Cretacic (Senonian) age rest. These are truncated and are overlain by horizontal Tertiary and younger strata. The Triassic and upper Cretacic beds are unconformable, which suggests a pre-Senonian uplift. The unconformity between the Senonian and Tertiary again suggests a later (post-Senonian) deformation.

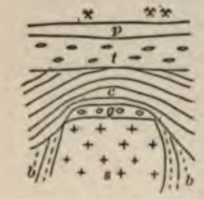

FIG. 113.

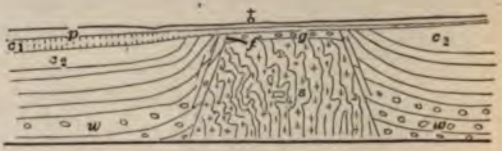

FIG. 114.

FIG. 113.—Section across "Aller Nord Stern" near Verden. *p*, Pleistocenic; *t*, Tertiary; *c*, Senonian; *b*, lower Triassic; *g*, anhydrite; *s*, Permic rock salt. (*After A. Tornquist.*)

FIG. 114.—Cross-section of the Rolfsbuettel salt-dome near Brunswick. *p*, Pleistocenic; *c*, Senonian; c_2, Comanchic; *w*, Wealden; *g*, gypsum and anhydrite; *s*, rock-salt with layers of clay, anhydrite, potash salts; *B*, basalt. (*After E. Harbort.*)

A third example is shown by the salt horst of Rolfsbuettel near Hillersee 13 miles northwest of Brunswick. This is illustrated in the section shown in Fig. 114 from Harbort.

The salt mass here is more than 6,000 feet deep, and is separated by outward dipping fracture planes from the enclosing Comanchic strata (Wealden and Neocomian) which are nearly horizontal a short distance away from the salt, but are strongly bent upward along the sides of the dome with additional fault planes. The enclosing strata are nearly 3,000 feet thick and the uplift of the plug through them appears to have occurred in lower Cretacic time, for the eroded Neocomian strata and the salt are covered by a thin layer of horizontal upper Cretacic (Senonian) beds sur-

[1] E. Harbort, Geologie d. nordhannoverschen Salzhutes, *loc. cit.*

R. Lachmann, Salzaufrieb, *loc. cit.*

A. Tornquist, Anschauungen über die Bildung der Kalisalzlagerstätten Deutschlands Industrie, 1906, Beilage No. 14, p. 93.

mounted in turn by Pleistocenic deposits. The surface of the salt is protected by a rather thick horizontal layer of residual gypsum and anhydrite as in the other occurrences. The salt mass itself is strongly contorted, so that it is impossible to identify the several layers of mother liquor salts.

About thirteen miles east of the last locality lies the salt dome of Fallersleben (Einigkeit shaft), a section of which is shown in Fig. 115.

The salt mass has the form of a very unsymmetrical anticline with steeply dipping sides and with a more extensive series of salt beds above the principal anhydrite (younger salt series) better preserved on one side than on the other. The upper part of the salt mass is covered by a residual layer of gypsum which here, however, is not horizontal, but also has an anticlinal structure. The salt occurs in the midst of more gently dipping middle Keuper and Rhaetic beds over which lie the strata of Liassic age. The enclosing series is strongly discordant with the salt strata, which would suggest a pre-upper Triassic uplift. It has, however, been definitely ascertained that no tectonic folding occurred in this part of Germany, between the Permic and upper Triassic time, and the uplift and folding of the salt beds as well as their penetration through and arching of the overlying strata must be of younger than Liassic age, the discordance between the Permic salt and the upper Triassic strata being the result of local upthrust of the salt strata.

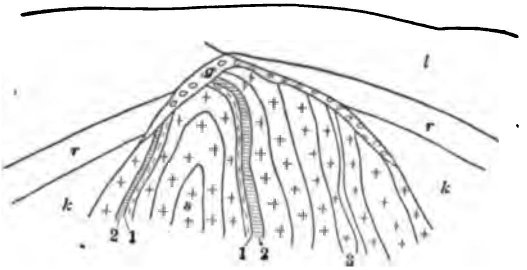

FIG. 115.—Cross-section of the "Einigkeit" salt-dome near Fallersleben. *l*, Lias; *r*, Rhaetic; *k*, middle Keuper; *g*, residual gypsum; 3, rock-salt with (1) hart-salt, (2) principal anhydrite, (3) carnallite. (*After H. Stille, Z. f. pr. Geol.*, 1911.)

Origin of North German Salt Domes.—Many of the early German writers (L. v. Buch, Hofman, Karsten, etc.) have explained salt domes (not then known from Germany) as magmatic matter intruded from below under tremendous gas pressure, but most of the recent authors who discussed the German domes have regarded them as due primarily to tectonic disturbances. Among these, Professor Stille has been one of the foremost advocates of the tectonic theory of origin, and he has given evidence for a succession of such disturbances in North Germany during middle Cretacic, early Tertiary, lower Miocenic, Pliocenic and perhaps even Pleistocenic time. Where the salt mass pierces the older of the superjacent strata, Stille concludes that there was a direct parting of the summit layers (Deckgebirge) over the salt in the axis of the anticline, and that the compact salt mass was pushed through this gap, so that it came to lie within the younger strata, which were correspondingly deformed. E. Harbort[1] has more recently advanced the hypothesis that the relatively plastic salt mass has been squeezed upward like a fluid magma under the pressure of orogenic forces pushing aside the overlying strata when they became fractured, and leaving them behind as the more inflexible masses. On the other hand, R. Lachmann is among the leaders advocating a purely endogenetic origin of these salt domes. He considers that it is only a step from the smaller, purely diagenetic deformations, such as are shown by the kieserite layers of the Stassfurt region (see Fig. 107) to the more pronounced metasomatic deformations, such as the solution and redeposition of some of the salts (as in the carnallite zones; see Chapter XXIV)[2] and finally the recrystallization of the salt mass during the separation of the several salts originally mixed by diffusive migration and the rise of the salt from the deeper regions under hydrostatic pressure. Under these influences the salt mass itself becomes deformed while at the same time it pierces the overlying strata, which also become deformed in the process.

It will be noted that the theories of formation of the salt domes advanced for the American occurrences by Hill and modified and elaborated by Harris, differ essentially from those mainly advocated for the North German salt horsts, while the theory advocated by Rogers for the American domes essentially conforms therewith. The American domes are explained by the authors quoted as deposits of salt from rising solutions, while the North German ones are regarded as deformations of original salt masses (Permic) known to exist in the region of embed, either through tectonic or through endogenetic forces or to a combination of both. It is not improbable that, as Rogers has argued, the American examples may also be cases of pure deformations of salt bodies underlying the Cretacic formations, though up to the present no such salt bodies have been discovered in regions other than those occupied by the salt domes. On the other hand, it is difficult if not impossible to explain the European occurrences on the theory of rising brine solutions, as these salt bodies show the normal succession of anhydrite, salt, and mother liquor salts, found in the undisturbed deposits of the same age elsewhere in the region. If the American domes are also cases of deformation, they must probably be regarded as formed from original salt deposits free from anhydrite and mother liquor salts, and possibly derived in the first place from connate sources. The two groups have in common the undisturbed or but slightly deformed gypsum or anhydrite cover, which is apparently a residual deposit concentrated from sulphate impurities in the salt itself, the upper part of which was removed by solution, either at the surface or within the zone of circulating ground waters. The relation of the salt mass to the enclosing strata is likewise similar in the two series.

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[1] E. Harbort, Richard Lachmann's Salzgeschwüre, Monatsber. d. deutsch. geol. Gesellschaft, 1911, p. 267. Also 1910, No. 4, pp. 340, 343.

[2] Lachmann, R., Natur des Everdingschen descendenten Hauptsalz Conglomerats. Monatsber. d. deutsch. geol. Gesellschaft, 1910, p. 318. See also F. Rinne, Umformung von Carnallit unter Allseitigem Druck; von Koenen Festschrift, Stuttgart, 1907, p. 369; and Plastische Umformung von Steinsalz und Sylvin, Neues Jahrbuch, etc., 1904, I, p. 114.

OTHER SALT DOMES

A salt dome of essentially similar character has long been known from Algeria, this forming the famous Rhang-el-Melah (Fig. 116). The salt mass is nearly circular in section, and it rises through strongly deformed Cretacic and Tertiary strata. Another example of this class is found in the salt hill of the Maros Valley in Hungary (Fig. 117) and still other examples are found on both sides of the Carpathians. They have been especially well studied in Roumania, where they are of significance in connection with the petroleum deposits. The salt dome of Cardona, Spain, appears to be another European example, while a number of them are found in various parts of Asia. All of these will be described more at length in their appropriate place in the stratigraphic chapters of this book (Vol. II). Some of them, as for example the Algerian domes, are closely associated with igneous activity, but for none of them has a controlling igneous force been positively demonstrated.

The Roumanian salt domes are confidently referred to a tectonic origin by Mrazec.[1] Here too the tendency of the salt beds is to pierce through the overlying rocks at certain points on the axes of anticlines, this in some instances resulting in the penetration of the salt core for more than 7,000 feet through the overlying sediments. Such a pierced fold has been termed by Mrazec, a *diapir fold* and the following diagram illustrates his conception of its development (Fig. 118). In many cases pro-

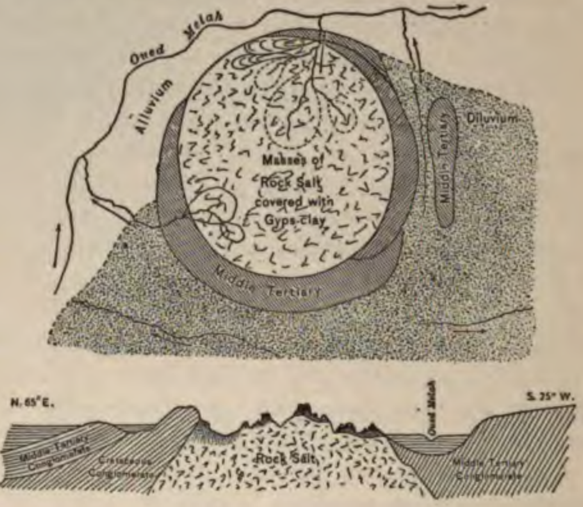

FIG. 116.—Map and cross-section of the Rhang-el-Melah salt-dome, Algeria. (*After M. Ville.*)

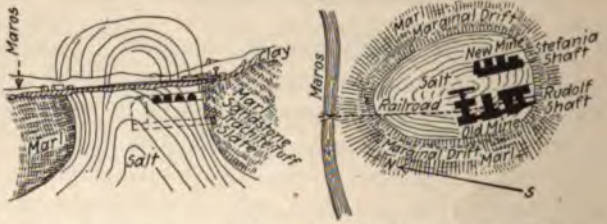

FIG. 117.—Section and map of the Salt Hill of the Maros River Region in Hungary.

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[1] Mrazec, L. and Teisseyre, W., Aperçu Geologique sur les formations saliferes et les gisements de sel en Roumanie Mon. des intérêts petrolif. Roum., Nos. 43–51, Jan.–June, 1902.

Mrazec, L., L'Industrie du pe'trole en Roumanie, Bucarest, 1910.

Mrazec L., Les plis à noyaux de percement., Bull. Soc. Sci. Bucarest, 1906.

nounced thrust faulting, probably of subsequent occurrence, has separated the salt core from the original bed, so that it now forms an isolated or unrooted mass, or Klippe (Mrazec).

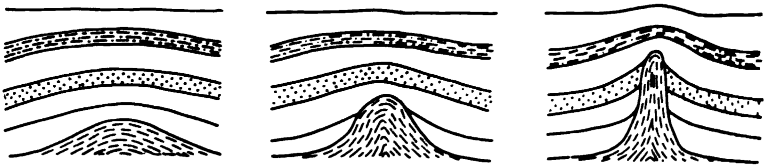

Fig. 118.—Development of the diapir structure of the Rumanian salt domes. (*After Mrazec from Rogers.*)

COMMON CHARACTERISTICS OF SALT DOMES

Following Hahn, we may sum up the characteristics which all known salts domes have in common, as follows:

1. A more or less circular section and cone-like or plug-like shape.
2. Isolated position of the salt mass.
3. General purity of the salt.
4. An apparent anticlinal or quaquaversal structure or at least, a very steep surface of the salt nucleus.
5. A usually sharp discordance between the salt mass and the surrounding strata.
6. Frequent minor deformations not explicable as the result of normal folding.
7. Stratigraphic independence of the salt mass with reference to a certain age or a certain horizon.
8. The secondary relationship which the salt core bears to the enclosing strata.
9. The more or less positive rise of the salt mass piercing, in some cases, thick formations.
10. The almost universal presence of a capping of residual gypsum or anhydrite.
11. The location of the domes along lines of tectonic disturbance, especially at the crossing of fault planes or the crests of anticlinals.

So far then, as we can judge from the characters of the known domes, exogenetic forces are not sufficient to produce all the characteristics, though they may account for many or perhaps most of them. For others, endogenetic forces must be appealed to, and these may be, in some cases, of great significance.

CHAPTER XVIII

CONDITIONS OF SALT DEPOSITION IN FORMER GEOLOGICAL PERIODS

Salt deposits were probably formed throughout all geological time, and those which have been formed since the beginning of the Palæozoic were probably in all essentials like those forming today, though their distribution was often different. This is primarily the case with the Palæozoic, during which era the zones of aridity had a very different distribution from that existing today, so much so, that the greatest of the Palæozoic salt deposits, the Siluric of America, and the Permic of Europe, lie in regions which today have a plentiful rainfall. With the beginning of Mesozoic time, however, the modern distribution of belts of aridity had come into existence, so that in general the Mesozoic and younger deposits are found in regions where salts are forming today or where they could form with a very slight modification of the physiographic or climatic conditions. The most satisfactory explanation which has so far been offered for this peculiarity of climatic distribution is a change in the position of the poles of the earth between Palæozoic and Mesozoic time, the position in Palæozoic time being one more or less diametrically opposed to that which was assumed at the beginning of Mesozoic time and which has continued with perhaps minor oscillations down to the present time. It should be noted, however, that this explanation is still a tentative one, and cannot be accepted as established until it has been tested by all the known facts of Palæozoic history.[1]

PERIODICITY OF LAND AND SEA EXPANSION AS AFFECTING SALT DEPOSITION IN THE PAST

Among the most important phenomena which have influenced the deposition of salts in former geological time, as well as their preservation after deposition, were the alternate sea and land expansions which have taken place in the past with sufficient regularity to enable us to recognize a certain periodicity. While many minor movements took place owing to local elevations or depressions of the land, the movements to which reference is here made were widespread, possibly universal, and are of the class to which the term Eustatic movements was first applied by Edward Suess. They are best described in terms of transgressions and regressions of the sea, and while our knowledge of them is largely confined to the present Northern Hemisphere there are not wanting indications that they were at least to some extent manifested in the southern hemisphere as well.

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[1] For further details see Grabau, A. W., "Principles of Stratigraphy," pp. 90–92, 891–900.

Positive Eustatic Movements.—This name is applied to a widespread advance or transgressive movement of the sea, in which the oceans creep over the shallow lands progressively submerging them and covering large portions of the continental masses with epireic seas, of comparatively shallow depths. Such movements are marked by regular advance of the shoreline and by a progressive overlap of marine strata in a landward direction[1] (Fig. 119). In such an overlap, each successively younger marine formation will extend beyond the preceding one, resting in turn upon the old land surface beyond the shoreward edge of the preceding formation. It is, indeed, by the overlap of successive marine formations that the geologist determines the progress of marine transgression in the past, and when he is able to determine that such overlap is not purely local but can be recognized for the same formations over an entire continent and better still over several continents, he is justified in concluding that he is dealing with a major or eustatic positive movement of the sea.

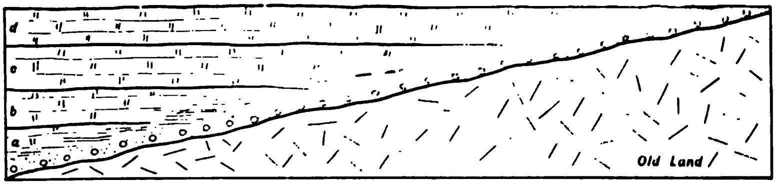

FIG. 119.—Diagram showing normal progressive overlap of a transgressive marine series. In all cases a basal sandstone or conglomerate rests directly upon the old land and merges laterally and vertically into other strata.

Causes of Positive Eustatic Movements.—What the causes of such movements are, may not be determinable; but if they can be shown to be worldwide they must be referred to a universal relative rise in sea level. Such a universal rise of sea level may be brought about by an increase in the quantity of water in the ocean, a phenomenon difficult to understand if not inconceivable except in so far as it takes place during very long periods of time. Or it may be accomplished by a shoaling of the abyssal depths of the sea through the formation of great submarine "rises" or up-bulgings which cause displacements of the waters and their creeping out over the lands. If such transgressions are confined to one of the continental blocks they may be due to the depression of that block, with the flooding of the low areas of this block by the sea. This would mean a general lowering of the sea level and a withdrawal of the waters from the other continental blocks where thus retreatal or negative movements of the strand-line would be inaugurated. Or again, it may be due to the rising of another continental block with accompanying displacement of the water which is spilled off the edges of the rising block. Reëstablishment of equilibrium would bring with it the spreading of the water over the low lands of the other continental blocks, *i.e.*, a transgressive movement. Another cause of transgressive movement may be the melting of huge continental ice masses, which not only furnish additional water to the sea, but by the cessation of their mass attraction would bring about a lowering of the sea level in their vicinity, while that in distant regions would experience a corresponding rise. Such a tilting of the sea level appears to have taken place during the existence of the great continental ice sheet in Pleistocenic time, and it has been estimated that on its disappearance the sea level in the tropics rose approximately 180 feet,[1] at least 30 feet of which was due to the flattening out of the sea level after the cessation of the attraction.

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[1] See "Principles of Stratigraphy," Chapter XVIII.

Finally, it may be noted that a migration of the earth's poles would bring with it a corresponding change in relative sea level. The difference in length of the polar and equatorial axes of the earth is 43 kilometers or nearly 27 miles. Thus if the equator should migrate, as it would with the migration of the poles, the equatorial bulge of the sea would migrate with it, and a submergence of the lands in that section would occur, with a concomitant emergence of the lands progressively invaded by the polar regions. If the former polar regions of the earth became equatorial regions, there would be a rise of water at the old polar points of nearly 13½ miles, with a corresponding change in all directions away from them. Conversely there would be a corresponding lowering of the water at the former equatorial points, thus usurped by the poles. Such changes in sea level would, of course, be neutralized after a time to a certain extent by a corresponding bulging or depression of the lithosphere. Where the migrations of the poles are of slight extent, a corresponding minor change of level will result, but this may be sufficient to cause considerable transgression over shallow lands. Whether the known migrations of the poles are of sufficient magnitude to produce such changes has not been ascertained.

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[1] Daly, R. A., Am. Jour. Sci., Vol. 30, 1900, pp. 297–308.

Determination of Overlap and Transgression.—It must not be assumed that the actual overlap of strata is always so well marked that it can be observed in a single section, though sections showing this are occasionally met with. Such minor overlaps are, however, no certain indication that great transgressive movements such as are here referred to have taken place. To determine such movements, successive sections of the same formations at points tens if not hundreds of miles apart must be studied. It then becomes necessary to determine definite stratigraphic horizons or levels, which can be recognized again in each of the sections studied so that it may be ascertained which portions of any given Section *A*, correspond to a determined portion of a distant Section *B*. Lithological features seldom serve this purpose, the only reliable horizon markers being the organic remains entombed in the marine strata. Not all organic remains are of equal importance, some having a much greater vertical range than others, and therefore not indicating definite horizons in the sections. Those that do indicate such horizons are known as Index Fossils, and they must be carefully ascertained for each formation and for each continent, or even for different parts of the same large continent.[1]

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[1] For descriptions and illustrations of the more important Index Fossils of North America, see A. W. Grabau and H. W. Shimer, North American Index Fossils, 2 vols., A. G. Seiler and Co., New York, 1909-10. For those of Europe consult Ernst Koken, Die Leitfossilien, 1896; Hermann Tauchnitz, Leipzig; and Georg Gürich, Leitfossilien, Berlin Bornträger Bros., 2 parts issued so far. Also the Lethæa Geognostica edited by F. Frech, Pt. I, Palæozoic (2 vols. complete), Pt. II, Mesozoic, Vol. I complete, others in course of publication. For greater details the palæontological literature of the several countries must be consulted. (See list of works for North America in Vol. II of Grabau and Shimer, North American Index Fossils, Appendix C.)

To make clear the use of such ascertained stratigraphic horizons in the determination of progressive overlap and positive sea transgression, the following diagram is inserted (Fig. 120).

Three sections, *A*, *B* and *C*, are studied in a given region, the first two one hundred miles apart, the third 50 miles beyond the second in the same direction, all of them beginning with crystalline rocks upon which lie sediments which by their contained fossils are recognized as former marine sediments now consolidated into rock. In Section *A*, three distinct stratigraphic horizons are recognizable by index fossils, these being named in order from below upward, horizons *a*, *b*, and *c*, respectively. In Section *B*, horizon *a* is absent, *b* and *c* alone being represented, *b* lying directly above the crystallines and *c* at about the same distance above *b* as in Section *A*. It is evident that there has been an overlap here, the formations characterized by horizon *a* being overlapped by that beginning with horizon *b*. If horizon *b* lies 1,000 feet above the crystallines in Section *A*, the overlap between the two sections is approximately measured by 1,000 feet of strata and from the nature of these strata, whether limestone or shale, some idea may be formed as to the approximate length of time consumed in the transgression of the sea over the one hundred miles from *A* to *B*. In Section *C*, horizon *b* is not found, while horizon *c* lies at an elevation above the crystallines equal to about half the distance between horizons *b* and *c* in both the other sections. Therefore, it may be assumed, other things being equal, that the amount of overlap between Sections *B* and *C* is measured by half the interval between horizons *b* and *c* in the two earlier sections, say by 250 feet.

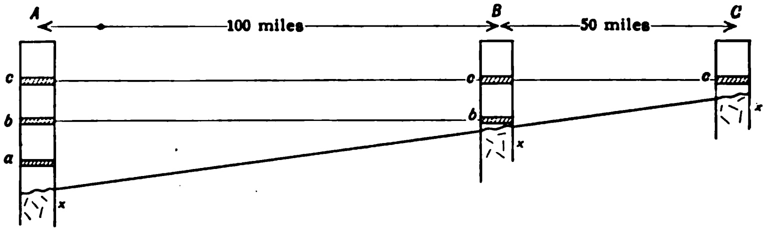

FIG. 120.—Hypothetical columnar sections taken at intervals of 50 and 100 miles to illustrate trangressive overlap of formations. (*For description see text.*)

It is hardly necessary to say that the problem is seldom as simple as here indicated. Indeed, often the determination of overlap requires a very detailed and prolonged study and involves the consideration of all of the available data. In such cases the problem can only be solved by the highly trained stratigrapher and palæontologist, but in many cases the problem is sufficiently simple to come within range of solvability by the nonspecialist.

Significance of Transgressive Movements in Terms of Salt Deposition.—The bearing of transgressive movements of the sea on salt deposition is very great. During periods characterized by such a movement, the formation of evaporation salt deposits comes almost to a standstill. To be sure, some evaporation deposits may form along the sea margin, and even extensive accumulations of terrestrial salts may take place in the interior of continents unaffected by such transgressions at least in its earlier stages. Salts formed along the sea coast, however, will soon be overwhelmed by the advancing waters and so become subject to re-solution before they are properly buried by a protective covering. Moreover, the aridifying effects of winds and desert areas in which salts may accumulate will be reduced to a minimum extent.

In conformity with these principles, it is a notable fact that evaporation salts are seldom met with to any extent in formations deposited during periods of great marine transgression, such deposits, especially those of continental origin, being most marked during periods characterized by sea retreat and continental expansion. Seashore salts are, of course, most extensively formed during periods of relative stability between land and sea.

While thus the formation of evaporation salts is reduced to a minimum during periods of sea transgression, the formation of precipitation and organic salts is greatly facilitated. For with the expansion of the sea comes also an expansion of organisms in the sea, and hence an abundant separation of lime from the sea water by these organisms. Moreover, as this lime is separated, the additional molecule of CO_2 which has kept it in solution is liberated and returns in large part to the atmosphere. Here it becomes an important factor in increasing the thermal density of the air, for it has been fully ascertained that in proportion as the air is charged with CO_2 will its power to prevent radiation of the heat from the surface of the earth be increased. Periods of sea expansion are thus periods of more or less universal amelioration of the climate, so that the growth and decay of vegetation, especially in regions of abundant rainfall, is accelerated. Thus acids are furnished to the land waters for further solution of limestones, and a continuous supply of lime in solution is furnished to the sea. This may locally increase to such an amount as to result in deposition from supersaturation. Where much decaying organic matter is found in the shallower portions of the sea, direct precipitation of calcium carbonate through the formation of ammonia salts may also be produced.

The transgressive movements of the sea become, however, of significance in inaugurating conditions favorable for the preservation of salt deposits formed around the margin of, and upon the land during the period o[illegible]ure preceding the transgression. Terrestrial salt deposits, [illegible]ose resulting from the evaporation of cut-off portions of th[illegible], if properly protected by a layer of impervious dust or a [illegible]t of scarcely soluble salt such as gypsum or anhydrite, will, [illegible]eing submerged beneath the encroaching sea be buried under strata of marine sediments and so be preserved for future exploitation. This has been the history of practically all of the more important salt deposits of former geological periods.

Negative Eustatic Movements.—These are the reverse of the positive movements, resulting in a withdrawal of the sea from the flatter portions of the land which by emergence enlarge the previously existing land masses. Such withdrawal of the sea in the past was at times sufficient to uncover portions still submerged at the present time, for it must be borne in mind that the littoral zone around the continents is in reality the submerged flat margin of the continental surface. It is only at the margins of the present continental shelves that the real rim of the oceanic basins is found. If our continents should suffer further emergence by lowering of the sea level, the retreat of the shoreline would be a comparatively rapid one over the flat continental shelf. This rapid retreat would come to an end when the edges of the shelf are reached, after which, with continued lowering of the sea level, where would be only a comparatively slow retreat of the shoreline down the steep continental slope.

Negative eustatic movements of the sea, if sufficiently long continued, are characterized by the progressive narrowing of the belt of deposition, each succeeding formation covering the older ones to a less extent than its predecessor did. A progressive off-lapping of formations is thus produced, which in transverse section would show the relationships depicted in Fig. 121.

In such a series, a greater number of formations or a greater thickness of the same formation would be found in the region last uncovered by the retreat, whereas in the region first uncovered only the lower formation or the lower members of a formation would be found. For example, in the retreat of the Beekmantown (Lower Ordovic) sea from the region of the present Mohawk Valley in New York to the region now forming Central Pennsylvania, a distance of one hundred miles, progressively higher members of the Beekmantown series were deposited toward the southwest, in which direction the sea retreated while by the retreat, the northern edges of the members already deposited, were successively exposed. Thus in the Mohawk Valley region, which might be represented at *C* in Fig. 121, only the lowest division (*a*) of the Beekmantown series, about 500 feet in thickness was formed, whereas in Central Pennsylvania all or nearly all of the members were deposited (*a–e* at *A*, Fig. 121), aggregating a total of 2,500 feet of strata. At some point intermediate between the two end points (as at *B*, Fig. 121), only one-half of the series was formed, this consisting of the lower members only.

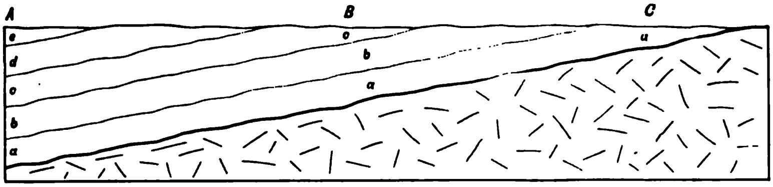

FIG. 121.—Diagram illustrating the "off-lapping" of strata during the retreatal movement of the sea.

Complication of the Process.—During the retreat of the sea, a certain amount of erosion of the progressively exposed strata may occur which renders the determination of the original amount of deposition at any given point of the retreatal series, a matter of some difficulty and tends to introduce inaccuracies. Such difficulties are eliminated where the edges of the retreatal series pass into material of another character, such as quartz sandstone, when the original formation is chiefly limestone and where the passage beds from the limestone to the sandstone are preserved as shown in the following figure (Fig. 122). Here the preservation of the passage beds will show that no appreciable amount of the retreatal series has been removed by erosion. The St. Peter sandstone, which rests upon the retreatal Beekmantown (Lower Magnesian) series of the Mississippi Valley region and in many places grades down into it, shows that little erosion of the older series had occurred before it was covered again by the advancing series of the transgressing sea in Middle Ordovicic time.[1]

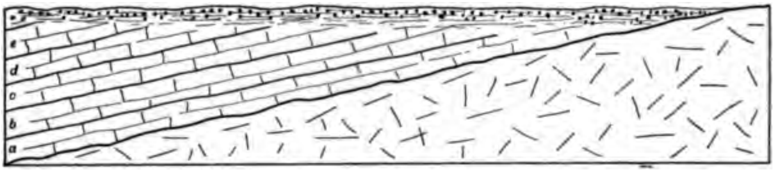

FIG. 122.—Diagram of an "off-lapping" series formed during a retreatal movement of the sea, with a capping "sandstone of emergence" into which the successive strata merge.

A second complication arises where continental sediments are deposited, either simultaneously with the emergence of the older series into which they will then grade, or after the emergence, during a period of prolonged land interval. The first of these cases is illustrated by the Catskill sandstone of Upper Devonic time, a continental formation deposited as a series of flood plain and delta formations, and which progressively replaces the corresponding marine Chemung series. This relationship is shown in the above diagram (Fig. 123). Such a replacement has been termed a replacing overlap, and it can readily be determined when the relative thickness of marine and continental

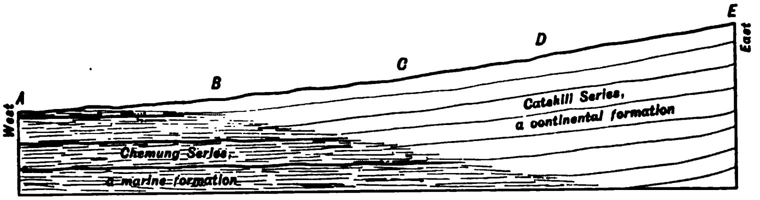

FIG. 123.—Diagram showing the replacing overlap of the continental Catskill series over the marine Chemung series. This indicates retreat of the sea shore with corresponding advance of the continental deposits.

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[1] For further details of this example see the author's paper, Types of Sedimentary Overlap, Bull. Geol. Soc. of America, Vol. XVII, and "Principles of Stratigraphy," p. 738.

beds are plotted in a series of sections across the State of New York, as indicated by the letters *A* to *E* in the diagram. Thus at *A* the entire series is marine, this being the case in the western part of the State of New York. At *E* the entire series consists of the continental Catskill rocks, as in eastern New York (Catskill Mountains). At points between these, *B* to *D*, successively greater thicknesses of continental rocks will rest upon successively thinner masses of the marine series. A replacing series of this type is not favorable for the formation of marginal sea salt deposits, owing to the instability of the sea shore. Nor are the conditions especially favorable for the formation of terrigenous salts since such a replacing overlap implies relative constancy of deposition of clastic material, a process unfavorable to salt formation.

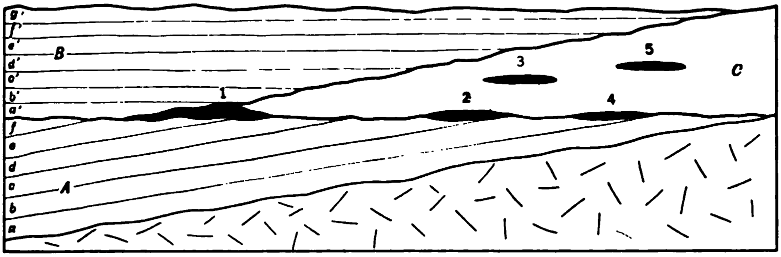

FIG. 124.—Diagram showing a retreatal marine series (*A*) covered in part by an advancing continental series (*C*) and a later transgressive marine series (*B*). During the retreat of the sea the conditions were favorable for the formation of the sea margin salt deposits (1, 2 and 4), which were partly covered by the continental deposit (*C*) in which continental salt deposit (3, 5) were also formed. Subsequently the entire series was covered by the transgressive marine series (*B*). On the left of the diagram the two marine series are separated by a hiatus and disconformity showing that the lower series was exposed for a time before it was again covered by the later marine series (*B*). All of the salt deposits here shown may also be of wholly continental origin, formed after the retreat of the sea.

The case is different when continental deposits are formed after the retreat of the sea and before its readvance. Such deposition indicates a period of static conditions between the two movements, and thus conditions favorable not only to the accumulation of terrigenous salts but also of sea-margin deposits are furnished. The advancing sea during the next period will bury such a deposit, provided it is protected from re-solution by a covering layer, and so enclose it between the two series of formations, the retreatal and the transgressive. This is the manner in which the Salina Salts of North America were enclosed between the lower and the upper marine Siluric formations, as will be discussed more fully in a subsequent chapter. The relationships of such deposits to the enclosing marine series is shown in the diagram (Fig. 124) on page 399, where it is seen that the continental salt-bearing series is by no means of the same extent as the enclosing marine series.

Causes of Negative Movements.—Negative eustatic movements of the sea are caused by conditions the reverse of those which produce the positive movements. These may consist in a deepening of the ocean basins and a consequent withdrawal of the waters from all the land surface. To some extent such withdrawal of the water may be effected by their accumulation as snow and ice upon the land mass, and by the attraction exerted by large continental ice masses. The withdrawal due to the latter cause would, of course, affect only regions remote from that in which the ice has accumulated. Migrations of the poles, which would result in submergence of the land in the equatorial regions, would result in emergence to a corresponding extent in the regions nearer the poles. Elevation of a continental block would result in the withdrawal of the waters from over the margins of that block, coupled with an advance over other blocks; while, conversely, depression of another continental block with accompanying submergence, would result in the withdrawal of the waters from the margins of the other continental blocks. Local emergencies may, of course, be due to warpings of the continental mass, but these are as a rule of minor significance though they become important in the production of a cut-off from the sea. Indeed, all cut-offs of any great extent, such as that of the Caspian and such as that which made possible the deposition of the great salt formations of North Germany (see Chapter XXIV) were produced by local warpings of the land.

Determination of Retreatal Series.—As in the case of the transgressive series, the retreatal one of wide extent can only be determined by a study of sections at considerable intervals. This is made sufficiently clear by the diagram, Fig. 121, given on page 397, where it is seen that in the region of earliest emergence at *C*, only the lowest member (*a*) of the series is present, whereas at *A* a series of higher strata (*b*–*e*) overlie the lower one, only the earlier of which, *b* and *c* appear above *a* in section *B*, intermediate between sections *A* and *C*. In the study of both transgressive and retreatal series it must be borne in mind that the formations of any given section may be deformed subsequently to deposition so that they will lie at an angle different from their original very slight angle of deposition, while in other sections the strata may be little or not at all deformed. This is indicated in the following three sections (Fig. 125), beneath which is given the restoration.

Significance of Retreatal Movements in Terms of Salt Deposits.—By the retreat of the sea, large areas of flat or slightly undulating land are exposed, and if these are situated within belts of arid climate they form favorable districts for the deposition of salts of both connate and decomposition origin. Moreover, where portions of former sea bottoms are uncovered, there are sure to remain areas of depression in which residual sea water remains, and this by evaporation will deposit its salt. According to the original depth and areal extent of such depressions, the resultant deposit will be large or small, and even a basin of moderate depth, provided it be extensive enough, will by concentration in a smaller area furnish a salt bed of considerable thickness. It is in such basins, as we have seen, as well as in the cut-offs due to tectonic disturbances, that mother liquor salts will be deposited in the last stages of desiccation, and conversely, when from the geological history of the formations enclosing a great salt deposit one can deduce that this salt was formed in a residual water body, one is justified in exploring this deposit for mother liquor

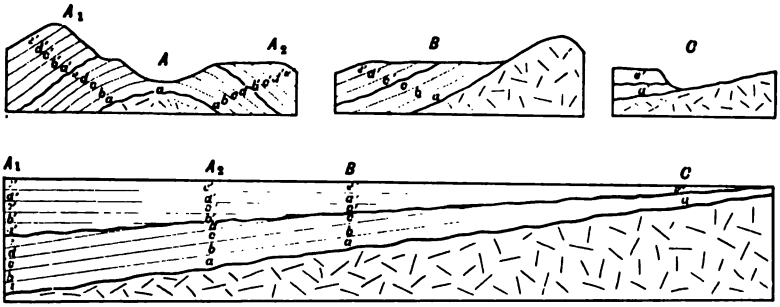

FIG. 125.—Three sections showing outcrops of strata in an anticline *A*, unicline *B*, and horizontal *C*. In each case the two series exposed are separated by a disconformity, which is greatest in *C* and least in *A*. The restored section beneath shows the conditions and relationships of these strata at the time of their formation.

salts. The application of this principle to some American salt deposits will be discussed in subsequent chapters.

While thus the conditions for the formation of evaporation salts become more favorable as the sea uncovers the land, the reverse is true for the formation of precipitation and organic salts. For as the area of shallow seas on the continental margin becomes decreased there is a restriction of the habitats of shallow water organisms which by their physiological activities secrete the lime from the sea water. If the sea retreats to the edge of the continental shelf, these organisms either become extinct or they must learn to adapt themselves to deeper water. Such adaptation would be a gradual one, for the retreatal movement is sufficiently slow to cover the life intervals of many generations of marine organisms. But even if many of these organisms should thus adapt themselves to deeper water, their number both as species and individuals will greatly decrease, nor will their activity in lime secreting be as great, as is abundantly shown by the thinner shells of deep sea mollusks and by the relative scarcity of lime deposits in the deeper parts of the modern oceans.

The decreased deposition of lime by marine organisms is accompanied by a decrease in the liberation of carbon dioxide, while conversely the expansion of the lands furnishes many areas favorable for the great development of plant life and the consequent depletion of the atmosphere of its carbon dioxide. Thus the air is rendered more permeable for the heat waves reflected from the earth's surface, and more extensive radiation will result with a corresponding lowering of the temperature. That this may have an important effect on further restricting life, can hardly be questioned.

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